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IRON, ALUMINUM AND MANGANESE IN THE SOIL SOLUTION OF HAWAIIAN SOILS

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A recent study of the methods of estimating and detecting acidity in Hawaiian soils (12) strongly indicates that the salts of iron, aluminum and manganese are involved.

Until recently the presence of free acid in acid soils was the only factor considered to be involved in their low fertility. In 1913 Abbott, Conner and Smalley (1) published results showing a definite relation between low root vitality of corn and an acid soil reaction. They found associated with this high acidity comparatively large amounts of soluble iron and aluminum salts. This work has been the incentive for numerous other investigations which have led to the suggestion that the toxicity of aluminum and manganese salts soluble in acid soils is of greater import than the hydrogen-ion concentration itself. The toxicity of alkali soils has long been attributed to the high concentration of certain alkali salts. It is interesting to note the more recent trend of soil acidity interpretations on the basis of injuriously high concentrations of acid-reacting salts.

In examining Hawaiian acid soils, the main characteristic, as in other acid types, is the absence of easily soluble calcium and magnesium salts and soluble. phosphates. Such conditions are conducive toward the accumulation of acid-reacting salts of iron, aluminum and manganese with free hydrogen ions formed by their hydrolysis in aqueous solutions, in spite of the comparatively high base and low silica content of Hawaiian soils.

In view of the recognized toxicity of certain concentrations of these salts in the soil solution a further study of the nature of these compounds seemed imperative. Both sugar cane and pineapples, the principal commercial crops of the Hawaiian Isands, have shown positive evidences of low root vitality on some of the highly acid soils.

OCCURRENCE

Aluminum. Aluminum occurs in Hawaiian soils chiefly as the phosphate, hydrate, oxide and silicate, the two latter compounds being also present in hydrated forms. It is the most abundant basic element. In both the lava and volcanic ash, aluminum is far in excess of iron and manganese and almost equal to the silica content if expressed as the oxide, Al_2O_3. During the process

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of disintegration the percentage of aluminum in the residual products is greatly
increased and still in large excess over all other elements except silica.   On
the basis of 30 per cent Al_2O_3 and calculated on the basis of 3,000,000 pounds
soil per acre foot there is present 900,000 pounds of alumina per acre.   It is
present in largest amounts in the clay and fine silt particles but even in the
coarser particles is often in excess of 20 per cent.

There appears to be some diversity of opinion as to the occurence of alu-
minum hydrates in mainland soils.   In fact this applies generally to all tem-
perate climates where environment induces kaolinization rather than lateriza-
tion.   Mirasol (14) has concluded, however, from a review of the literature
that there is evidence of their presence in some mainland soils.   The three
recognized hydrates of aluminum are; Diaspore, Al_2O_3 H_2O; Bauxite, Al_2O_3
$2H_2O$; and Gibbsite Al_2O_3 $3H_2O$.   The two former are insoluble in dilute
acids, alkalies and water, while Gibbsite is soluble in dilute acids and alkalies
but insoluble in water.   We therefore look upon Gibbsite as the principal
source of soluble aluminum.   In applying these facts and theories to Hawai-
ian conditions it is significant that in our yellow soils which are in a higher
state of hydration and in other types which are high in water of hydration,
aluminum is present in larger quantities soluble in dilute acids.   Tropical
environment is known to induce a higher concentration of Gibbsite in the
residual products of disintegration.   There is, accordingly, good evidence
of the presence of this hydrate in a large percentage of our island soils.

We also have strong evidence of the presence of aluminum silicates and
alumino-silicic acids which are more or less soluble in water and by dissocia-
tion the latter will yield hydrogen ions to a small degree.   We have present,
therefore, a large reserve of potential acidity.

Iron.   Iron like aluminum occurs chiefly as silicate, oxide (principally
ferric), and hydroxide.   The iron content of the lava and volcanic ash is
much lower than aluminum and approximately equal to the lime and mag-
nesia, usually being about 10 per cent.   It is greatly increased in the residual
products of disintegration but is still much lower than the aluminum content
of the soil.   The soluble salts of ferric iron are much less stable than those of
aluminum their hydrolysis and precipitation being, under soil conditions,
proportionately more rapid.   In our highly puddled and poorly aerated soils
ferrous salts are usually present in varying amounts.

Manganese.   Manganese occurs chiefly as the silicate and oxide widely
scattered in all soil types in amounts varying from a few tenths of one per
cent to 10 per cent.   It is present in the lava and volcanic ash in only small
amounts being rarely as high as 1 per cent and usually about 0.5 per cent.
During the process of disintegration it appears to be readily dissolved and
that present in the residual products is greatly reduced by weathering agents.
For this reason the island soils are proportionately lower in manganese than
the lava except in certain isolated lower areas of the aluvium where soluble
manganese salts have accumulated and precipitated as the dioxide, often as
high as 10 per cent.

Veitch (17) in a study of the Hopkins method of determining soil acidity was probably the first to call attention to the rôle of aluminum salts in acid soils. He noted the presence of aluminum in the extract obtained by shaking an acid soil with a solution of potassium nitrate. This solution of aluminum was attributed to the replacement of aluminum by potassium in the alumino silicates. Parker (15) concludes that this solution is due to a side reaction and the solvent of acid formed by the selective absorption of the basic ion of the salt solution. Additional theories of the source of soluble aluminum in the soil solution involve that of Ames and Boltz (2) who attribute its solution to the acidity resulting from sulfofication and that of Abbott, Conner and Smalley (1) who suggest the formation of aluminum nitrate in the absence of adequate lime to neutralize the nitrate formed during nitrification. On the other hand we note that Denison (7) failed to identify soluble (crystalloidal) salts of aluminum in soil extracts but did establish the presence of the hydrosol aluminum hydrate. Knight (12) also arrives at the same conclusion. Both question the formation of soluble salts of these elements in many acid soils.

The above contradictions suggested the need of clarifying some of these questionable points in Hawaiian soils and definitely determining the hydrogen-ion concentration at which we can have a reasonable assurance of the presence or absence of the salts of these elements. In view of the apparent relation between some types of root rot and soil acidity it is highly esential to be able to recognize more definitely the soil types on which this association is possible. So called root rot of sugar cane in Hawaii is not confined entirely to acid soils.

EXPERIMENTAL

The logical procedure in the separation of colloid from crystalloid compounds involves the utilization of a semipermeable membrane. The plan of the experiment was therefore as follows. A definite selection of soils was made to cover a number of characteristic types. The soil solution itself as well as salt solution extract were prepared and dialyzed for a definite period and the resultant changes in the soil solution determined.

Choice of soils

Soil 1. A yellowish brown silty clay from Kaneohe District, Island of Oahu. Pineapple plants badly wilted, sugar cane had previously failed.

Soil 2. A brown silty clay loam from Kaneohe District, Island of Oahu. Pineapple plants badly wilted, sugar cane had previously failed.

Soil 3. A bluish grey adobe soil, Waimanalo District, Island of Oahu. A low poorly drained soil on which a resistant cane variety grows well.

Soil 4. A dark grey sandy loam, highly organic, from Honokaa, Island of Hawaii. Sugar cane root vitally very low.

Soil 5. A dark grey sandy loam, highly organic, from Honokaa, Island of Hawaii. Growth of cane only fair.

Soil 6. A chocolate brown silty loam, highly manganiferous (7 per cent MnO_2). No indication of poor root growth.

Soil 7. A dark clay loam, from Experiment Station plots Honolulu. Good root growth.

Soil 8. A black clay soil from Waimanalo, Oahu similar to no. 3 but sufficiently impregnated with lime to make alkaline.

Experiment 1

Potassium nitrate extracts

Four hundred grams of soil were shaken, with 1 liter of a normal solution of KNO_3, continuously for three hours in an end-over-end shaking machine; 250-cc. aliquots of this filtrate were used for analysis. One was analyzed direct while the other was placed in a pyralodion sack. The sack and contents were suspended in an 800-cc. beaker, distilled water added to a level

TABLE 1

Analyses of KNO_3 extracts before and after dialysis

SOIL NUMBER	ORIGINAL EXTRACT					NON-DIFFUSIBLE EXTRACT			
	Reaction	SiO_2	Fe_2O_3 Al_2O_3	Mn_3O_4	CaO	SiO_2	Al_2O_3 Fe_2O_3	Mn_3O_4	CaO
	pH	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*		
1	4.46	0.0043	0.0809	+*	0.0350	0.0020	0.0030	—*	—*
2	4.46	0.0045	0.0106	+	0.0443	0.0000	0.0015	—	—
3	4.93	0.0115	0.0199	+	0.4480	0.0000	0.0015	—	—
4	5.39	0.0020	0.0019	+	0.1129	0.0000	0.0004	—	—
5	5.98	0.0045	0.0027	—	0.1806	0.0000	0.0017	—	—
6	6.00	0.0110	0.0018	—	0.2422	0.0009	0.0015	—	—
7	7.76	0.0050	0.0018	—	0.3794	0.0029	0.0012	—	—
8	7.90	0.0023	0.0016	—	0.6230		0.0016	—	—

* + present but not determined quantitatively; — not present.

above that of the solution within the sack and the whole placed in a water bath. This bath was maintained at temperature of 45°C. and the water in the beakers changed daily for a period of two weeks. At the end of this time the solution remaining in the dialyzing sack was subjected to the same analytical procedure as the original extract. The results are given in table 1.

All extracts were evaporated to dryness on the steam bath and heated in the hot air oven at 120°C. to dehydrate the silica. The acid insoluble residue from this operation was weighed as silica. Iron and aluminum were determined together as phosphates and precipitated in the presence of acetic acid in order to avoid calcium contamination. Manganese was not determined quantitatively.

The results definitely prove the presence of crystalloid forms of iron, aluminum and manganese in all the soils having pH value below 5.9 and indicate that at pH values above 6.0 only the hydrosol forms are present while the manganese is entirely absent. It should be noted that soil 6 contains as

much as 7 per cent MnO_2. Dialyzable forms of silica are present in all the soils and little or no colloid forms are present in solution. Manganese and calcium are present entirely in dialyzable forms.

In addition to the data taken for table 1 titrations of the KNO_3 extracts were also made on the original extract and the contents of the paralodion sacks after dialyzing for two weeks. In this titration 125 cc. was boiled for ten minutes and then titrated with 0.2 N KOH using phenolphthalein as an indicator. All the extracts within the paralodion sacks were practically neutral. The titrations in cubic centimeter of 0.2 N KOH are given in table 2.

TABLE 2

Showing titration of KNO_3 extracts as cubic centimeter 0.2 N KOH per 125 cc.

SOIL NUMBER	ORIGINAL EXTRACT	NON-DIFFUSIBLE EXTRACT
	cc.	*cc.*
1	6.00	Neutral
2	1.10	Neutral
3	2.60	0.05
4	0.80	Neutral
5	0.60	Neutral
6	0.10	0.10
7	Alkaline	0.10
8	Alkaline	Neutral

These results definitely show the acid or acid salts present in the KNO_3 extracts to be present in a form which will penetrate a semi-permeable membrane in entirety.

Experiment 2

The soil solution was next obtained from this same set of soils and dialyzed according to the following procedure. Five pounds of soil were added to each of five glass percolators, distilled water added to saturation and the

TABLE 3

Showing analysis of 1 liter of soil solution before and after dialysis

SOIL NUMBER	ORIGINAL SOIL SOLUTION					NON-DIFFUSIBLE SOLUTION			
	Reaction	SiO_2	Fe_2O_3 Al_2O_3	Mn_3O_4	CaO	SiO_2	Fe_2O_3 Al_2O_3	Mn_3O_4	CaO
	pH	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*		
1	4.46	3.6	7.2	0.8	30.9	0.8	1.6	—*	—*
2	4.46	10.5	15.1	18.3	116.9	0.8	4.4	—	—
3	4.93	66.5	10.0	4.0	117.2	0.8	1.2	—	—
4	5.39	19.1	8.2	3.3	550.4	0.4	3.2	—	—
6	6.00	16.5	0.8	0.0	29.6	...	...	—	—
7	7.76	27.7	4.0	0.0	91.1	2.0	3.6	—	—
8	7.90	41.2	3.7	0.0	274.4	0.4	3.6	—	—

*— not present.

whole allowed to stand for forty-eight hours. They were then treated by the displacement method as outlined by Parker (14) which had previously been shown to yield the actual soil solution when applied to Hawaiian soils. In this case distilled water was used as a displacing liquid. The first 200 cc. of percolate was collected from each making a total of one liter. Two hundred and fifty cubic centimeters of this soil solution was placed in paraloidion sacks and dialyzed as described in experiment 1. The remaining 750 cc. was analyzed direct. The results are given in table 3. It should be mentioned that this solution is probably less concentrated than the actual soil solution owing to the addition of water up to the point of saturation, but the results are comparable and serve well for determining the diffusibility of the components of the soil solution.

These results compare very closely with those obtained by extracting the soil with a solution of KNO_3. The iron and aluminum are present in largest part in the crystalloid form in all the soils having pH values of 5.5 or less while the manganese was not present in the soil solution with a pH value of 5.9.

<div align="center">DISCUSSION</div>

In view of the results obtained in the preceding experiments it is interesting to compare with similar investigations. Knight (12) in a study of the Hopkins method, subjected the KNO_3 extract to dialysis in a collodion sack. In his experiments 74 per cent of the titratable acidity passed through the membrane but no aluminum. All the latter remained in the collodion sack showing it present entirely in colloid form. The pH value of this soil is not given but it showed a higher titratable acidity than any used in these experiments. Similarly Denison (7) in leaching several Illinois soils with normal KNO_3 solution obtained no dialyzible aluminum salts. Therefore he concludes a single treatment of the soil with KNO_3 solution yields only the hydrosol aluminum hydrate. On percolating water through this soil he was unable to obtain a test for aluminum from five liters of percolate. Unfortunately he does not give the pH value of the acid soils used.

On the other hand Mirasol (14) found that by leaching acid soils with normal KNO_3 solution he was able to remove a large percentage of the iron, aluminum and manganese salts and effect a corresponding reduction in acidity. Similarly with water he noted a marked reduction of acidity corresponding with the removal of soluble salts of the above elements. His work has been severely criticized in view of the fact that he based his conclusions on the analysis of the soil before and after treatment. He therefore failed to distinguish definitely between colloid and crystalloid forms and did not actually demonstrate the presence of soluble salts.

Abbott, Conner and Smalley (1) determined the aluminum in the leachings from an acid soil in which corn roots were badly rotted but did not distinguish between crystalloid and colloid, assuming the former. Hartwell and Pember

(9) did not analyze the soil extracts but determined the toxicity of diffusible and non diffusible portions. Ruprecht (15) found iron and aluminum salts in acid soils of low fertility after filtering through unglased porcelain. Blair and Prince (3) have also determined iron and aluminum in water extracts of acid soils without attempting to distinguish between crystalloid and colloid forms.

It is evident from the above that there is more or less difference of opinion as to the forms in which iron and aluminum salts are present in the soil solution and some positive results supporting the non-existence of crystalloid forms.

From the data given in tables 1 and 3 coupled with other observations it may be definitely stated that all Hawaiian soils with pH values below a point between 5.5 and 6.0, believed by the writer to be 5.8, contain soluble salts of iron, aluminum and manganese. Whether these are toxic toward plant growth will depend upon associated environment more especially the available phosphates present in the soil.

It is hardly believed from the results thus far obtained that soluble iron salts are a factor of toxicity. While no attempt has been made in the analysis of the soil extracts to separate iron and aluminum it was possible to judge from the color of the precipitate the relative amounts present. Aluminum was present in excess in every case. Iron salts hydrolyze more rapidly under soil conditions and precipitate as $Fe(OH)_3$. It may be of interest to state that in attempting to prepare nutrient cultures for studying the toxicity of iron salts, it was found impossibie to keep iron in solution even at a concentration of 0.0002 N. These facts strongly indicate the minor role which iron must play in any toxicity of our acid soils. This refers only to ferric salts. Frequent instances have been noted in Hawaiian soils where puddled and poorly aerated areas have been found to contain appreciable amounts of ferrous iron. Such soils are usually characterized by a bluish grey color.

Of the soluble salts found associated with acid soils, aluminum has been found to be the most toxic and for this reason the reduced growth of many plants on such soils has been attributed to the presence of salts of this element in the soil solution. In our highly organic soils the aluminum appears to be present in large measure as organic salts of high potential, yet low intensive acidity. The solubility in dilute acids is very high with comparatively low solubility in water. Burgess (4) has published a method for the determination of aluminum in which he classifies aluminum soluble in 0.5 N acetic acid as "active." Applying this method to Hawaiian soils some have been noted as over 2000 parts per million while an even higher content of active iron has been noted in highly puddled soils. Analytical evidence therefore strongly indicates the presence of toxic amounts of aluminum in many of our acid soils.

The solubility of manganese is of special interest in its relation to the chlorotic condition of pineapple plants and the absence of chlorosis of sugar

cane grown on the manganiferous types. The principal physiological disturbance is, according to Kelley (11) due to an abnormal absorption of calcium by the plants grown on the manganiferous soils while Johnson (10) claims a toxic effect from manganese. No manganese soils have been noted by the writer with a pH value below 5.9 and no manganese has been found present in the soil solution at this pH value or higher. Soil 6 is a typical manganiferous type. The theory advanced by Kelley (11) suggesting the higher assimilation of calcium appears the more tenable, sugar cane having a greater tolerance for calcium. The lower acidity which is typical of the manganiferous type and below the hydrogen-ion concentration at which manganese salts have been found present in the soil solution and the greater absorption of calcium by plants on this soil type makes the toxicity of manganese appear less tenable at this reaction. This does not deny the toxicity of manganese salts but merely points out their absence in the soil solution of this soil type. If manganese does exert a direct toxic effect as noted by Johnson (10) with pineapples grown in water cultures, we must associate this with soils of higher acidity in which their presence is definitely shown by the data in tables 1 and 3. The influence of this factor on the growth of sugar cane is now being studied. Thus far there has been no evidence of any injurious nutritional disturbance with sugar cane grown on manganiferous soils. There is also no evidence of so-called root rot of pineapples on the manganese soils but only a chlorotic condition of the leaves attributed as above to the abnormal assimilation of calcium. There is, however, positive evidence of low root vitality of both sugar cane and pine-apples on some acid soils. All the soils of a pH value of 5.5 or lower contain appreciable amounts of manganese in solution and it is not unreasonable to suspect a certain degree of toxicity on such types.

Carr (5) in studying the relation of manganese to soil acidity or toxicity which terms he suggests as synonymous, claims the presence of soluble manganese at pH values up to 7.9. He bases his conclusions upon the work of Greenfield and Buswell (8) and the results obtained by himself using the Comber method of testing for soil acidity. Carr studied the precipitation of manganese as hydroxide using a fixed alkali, sodium hydroxide, and found precipitation complete only at pH 7.9. That this does not hold true under soil conditions is shown by the results given in tables 1 and 3. Manganese soils in Hawaii are usually found in localized areas formed by the deposition of manganese as dioxide. Evidence indicates it to be present in the lavas in a form easily dissolved by the agents of disintegration. It is therefore percipitated at an acidity for greater than pH 7.9 if we are justified in accepting the present pH value of these soils as a criterion. This high concentration of manganese dioxide in localized areas and the absence of manganese in the soil solution of the soils more alkaline than pH 6.0 may be attributed to precipitation by lime or the formation of manganic salts of extremely low stability which will not remain in solution.

Comber (6) found that on shaking an acid soil with an alcoholic solution of KSCN he obtained a red color, ferric sulfocyanate, and suggested the use of this reagent in testing the soil reaction. Carr (5) in a study of this method noted the formation of a green color which he attributed to the presence of soluble manganese.

The writer has also obtained this green color with all soils with reactions of pH 5.5 to 7.0 and with most soils of pH values above 7.0. Among the soils which Carr examined was a highly manganiferous sample from Hawaii in which he claims the presence of soluble manganese, basing his conclusions on the green color obtained by the Comber test. While he does not state the reaction of this soil it seems reasonable to assume that it is approximately pH 5.9 or higher in view of the fact that the writer has failed to find a sample of this type below this figure. Being at a loss to explain Carr's conclusions after having failed to find soluble manganese in soils of this type and reaction some attention has been given to a study of this point.

Most Hawaiian soils contain at least 0.5 per cent manganese dioxide and will range from this up to 10 per cent. A soil with a reaction of pH 5.5 or higher, regardless of the amount of manganese dioxide present, usually gives a greenish-blue color, not immediately but only on standing, by the Comber method using ethyl alcohol as the solvent. Soils with a pH value of 5.5 or less will retain their original red color. The writer believes, although it has not been absolutely proved, that there is strong evidence that this green color is due to the formation of manganese perchloride ($MnCl_4$). This suggestion is based upon a brief study of this color development, the fact that manganese is present in our soils principally as MnO_2, the anhydride of tetravalent manganese hydroxide [$Mn(OH)_4$], and further that manganese tetrachloride is one of the very few green manganese salts soluble in alcohol.

In determining why the green color, which appeared to be associated with the presence of manganese, is obtained with soils containing no soluble manganese it was necessary to recognize the results given in tables 1 and 3 showing no soluble manganese or other acid salts in the soils of pH 6.0 or higher in the KNO_3 extracts. That is, there was no displacement with potassium nitrate under the conditions of this method.

In treating a manganiferous soil containing 10 per cent MnO_2 by the Comber method a faint pink color was obtained, as usually noted, fading to colorless and finally to greenish blue on shaking several times and allowing to stand. The original pH value of this soil was 6.3 which on shaking with alcoholic KSCN dropped to pH 5.5 which is within the range at which manganese salts are in solution. In order to obtain further data on the increase in hydrogen-ion concentration when shaken with this reagent a series of soils was selected varying in reaction from pH 4.4 to pH 8.0. These soils were shaken with alcoholic KSCN in the proportion of one part soil to two parts 5 per cent KSCN in alcohol and the pH values of the mixtures determined immediately at intervals for twenty-four hours. In all soils of pH 5.9 or

higher the reaction dropped to pH 5.5 and gradually changed to a greenish blue color. In the more acid soils the reaction dropped considerably below pH 5.4 and all these retained their red color. In other words the soluble manganese which Carr found is not actually present in the soil solution as such but is made soluble by the higher hydrogen-ion concentration. On adding an excess of MnO_2 to the alcoholic extracts of all the soils which retain their red color the hydrogen-ion concentration will lower rapidly to pH 5.5 or slightly higher discharging the red color. The color therefore appears to be a function of the hydrogen-ion concentration. This is further indicated by the fact that a filtered Comber extract which is green will change to a red color on slightly increasing the hydrogen-ion concentration.

SUMMARY

Normal potassium nitrate does not displace the aluminum in aluminum silicates except in those soils with pH values below 6.0.

Soluble crystalloid salts of iron, aluminum and manganese were found in soils with pH values below 5.8.

At pH 6.0 or above manganese is not present in the soil solution and iron and aluminum only as the hydrosols of ferric and aluminum hydrates.

The solubility of manganese as indicated by the Comber test is due to the greater hydrogen-ion concentration developed on shaking a soil with alcoholic potassium sulfocyanate.

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ALKALI SOIL INVESTIGATIONS: II. ORIGIN OF ALKALI SOILS; PHYSICAL EFFECTS OF TREATMENTS[1]

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The presence of alkali in soils was observed and methods of reclamation studied long before scientists were able to account for their origin. Even today considerable difference of opinion exists as to their mode of formation. It has been pointed out (14) that during the last few years some of the investigators in the United States and Europe, especially Russia, have attacked the problem. In general the theories advanced go back to the researches of Way (27), Van Bemmelen (26), Lemberg (17) and others. We shall consider the theory of the Russian investigator Gedroiz (5, 6, 7, 8), whose papers are unavailable to American workers and which deserve more detailed review because of the important contributions to the phenomena in question. He recognizes that there are no such minerals as zeolites in soil, but on account of historical and general use of the term he adopts it in his discussion. He defines, however, what he means by zeolites of soil:

We understand as the zeolitic portion of the soil the aluminum silicate complex, which is capable of exchanging its bases for bases of salt solutions. . . . . When a soil is brought into contact with NH_4Cl solution the base is absorbed[2] by the zeolitic portion, bringing into solution calcium and magnesium. The amount of the chlorine ion is not changed in the supernatant or filtered solution. In general the amount of calcium and magnesium found in solution is equivalent (expressing the quantities in gram-equivalents) to the amount of ammonia lost from the solution. In some cases, however, the amount of ammonia absorbed is greater than the amount of calcium and magnesium brought into solution. The quantity of chlorine ions is not changed and this imparts to the solution an acid reaction.

These soils Gedroiz calls "soils unsaturated with bases." Soils in which the basic exchange is the same he calls "soils saturated with bases."

When the proper amount of concentration of NH_4Cl solution is used, the reaction is completed in one minute. This fact gives a better insight in the phenomenon of mutual exchange of ions and a clearer understanding of the nature of the zeolitic portion. In ordinary chemical reactions between a slightly soluble substance and one that is completely

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[2] Gedroiz uses the term absorption although he recognizes that the reactions are surface reactions; this would indicate the more generally known term adsorption.

soluble, as between $CaCO_3$ and sodium phosphate, the reaction does not go to completion at once; it takes days.

Gedroiz sees a close analogy between the reaction of the slightly soluble $CaCO_3$ with the easily soluble Na_3PO_4 and the reaction between the zeolitic portion of the soil with NH_4Cl. In the first case the product is insoluble $Ca_3(PO_4)_2$ and in the second case, the zeolitic portion in which NH_4 took up the place of the Ca and Mg. Gedroiz claims that "In the system, soil + NH_4Cl solution, the reaction speed is due to the surface nature of the reaction between the zeolitic portion and NH_4Cl, or the surface layer of the zeolitic portion. That the calcium and magnesium ions come from the insoluble portion of the soil may be demonstrated by the fact that a water extract contains none or very little calcium or magnesium." In a recent note (9) Gedroiz suggests the use of 0.05N HCl instead of NH_4Cl. The principle is that any cation may replace the cations of the zeolitic portion and hydrogen is a very powerful cation in this respect. In soils where the zeolitic portion is not saturated with metallic cations (in the earlier portion of the article Gedroiz calls it unsaturated with bases, as indicated above), hydrogen ions take their place. Such an unsaturated condition may be obtained by treating a saturated soil with a small amount of HCl of low concentration such as 0.05N.

In connection with the work of Gedroiz it is well to recall the work of Lemberg (17) who proved conclusively that many other silicate minerals have the same properties of base exchange in salt solutions as the zeolites. He showed that treating leucite with a sodium chloride salt solution converted it into analcite, which with potassium chloride could be converted back into leucite. His experiments show that sodium silicate minerals are less stable in salt solutions than the corresponding potassium minerals; in other words under similar conditions potassium will replace sodium more easily and more completely than sodium will replace potassium. This is suggestive on account of the well known facts that potassium is strongly absorbed by soils while sodium is not, and that the ocean is a solution of NaCl rather than KCl.

Gedroiz points out that the energy with which different cations force out from the soil the zeolitic bases, or the energy of absorption, is a function of the valence and the atomic weight of the cation. The only exception is the ammonium ion and Gedroiz (8) finds no explanation for it. As a matter of fact, this ion behaves just like the potassium ion in its energy of absorption and this is in accord with the octet theory as outlined by Langmuir (16), where he shows that K and NH_4 have a great deal in common. The similarity in behavior of K and NH_4 has been noticed by Loeb (19) and also by one of the authors (12, p. 72). Gedroiz continues:

The energy of absorption determines its persistence in the zeolitic portions of the soil. Among the cations of the zeolitic portion and the soil solution, calcium which possesses the highest energy of absorption, will persist in the zeolitic portion for the longest time. The composition of the zeolitic bases in soils which, for some reason, have become salinized

is brought about in a different way. Among the salts found in such soils, we recognize sodium, magnesium and calcium. If sodium salts prevail, we call the condition a sodium alkali; if magnesium, a magnesium alkali, etc. The presence of these salts in solution will have an effect also on the solid phase of the soil, since the mutual exchange outlined above will take place. In soils with a predominance of sodium salts the sodium cation will find its place in the zeolitic portion. This is of great importance since the leaching out of the excess of soluble salts will still leave the zeolitic portion saturated with sodium which will at any moment give up its place to any other cation which has a higher energy of absorption.

On the strength of the above considerations Gedroiz tries to establish the mode of formation of black alkali soils. If a soil containing soluble sodium salts saturated with the sodium cation shall also contain CaCO₃ the conditions as pictured by Gedroiz are as follows:

The soil solution will contain the ions of calcium and sodium; if the salinizing is appreciable and the concentration of sodium salts in solution is high, then the presence of the Ca ion in solution will not hinder the Na ion from entering the zeolitic portion of such a soil, forcing out |more Ca and Mg, since the concentration of the calcium ion in soil solution cannot be high due to the low solubility of CaCO₃. If for some reason or another the soluble salts of such a soil have disappeared we still have left the CaCO₃ and also much sodium in the zeolitic portion. Until the concentration of the sodium salts was high in the soil solution, the Ca ion on account of its small concentration can not hinder the sodium ion from entering the zeolitic portion, notwithstanding the higher energy of absorption of the Ca ion; under such conditions the Ca ion can not compete with the Na ion and replace it in the zeolitic portion. However, as soon as the excess of soluble salts disappears or their concentration is lowered, the Ca ion begins to force out the Na ion from the zeolitic portion. The equations for this reaction may be as follows:

$$\text{Zeolitic sodium} + CaCO_3 \leftarrow \text{zeolitic calcium} + Na_2CO_3$$
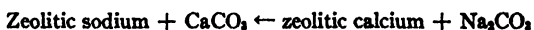
Zeolitic sodium + Ca(HCO₃)₂ ← zeolitic calcium + 2NaHCO₃. Thus sodium carbonate is formed when the soils contain zeolitic sodium and calcium carbonate.

On the basis of this theory, the addition of any soluble salt of sodium prevents the formation of sodium carbonate since the preponderance of the sodium cation prevents the calcium cation from entering the zeolitic portion and thus leave behind the carbonate.

Gedroiz (5) claims that wherever an abundance of chlorides and sulfates are present there is no soda. This is in apparent contradiction with the facts of the condition of the alkali soils used in the experiments reported in these papers. These soils contain tremendous amounts of chlorides, considerable soluble sulfates and even some soda. There is the possibility, however, that this condition may be looked upon as a transition stage in the process of black alkali formation. That the soil in question is not a true black alkali soil is apparent from the analyses and the color of the salts accumulating on the surface. The theory of Gedroiz demands that the soda formation is the second stage in the process of black alkali formation: first comes the salinizing process (solontzhak in Russian) then comes the desalinizing stage followed by the appearance of the zeolitic sodium and formation of soda (solonetz in Russian).

This theory differs from the prevailing opinion in the United States as formulated by Hilgard (11). According to Hilgard, the sodium carbonate is a result of the exchange of the sodium compounds and calcium carbonates existing in the soil solution. Gedroiz also postulates that the zeolitic portion in order to react with cations of the soluble salts does not go into the solution stage; the reaction is an absorption phenomenon and in the light of our modern knowledge of physical chemistry especially in the realm of colloidal chemistry this is quite reasonable. Gedroiz differentiates physical absorption from physico chemical; the former consists of absorption from solution without an exchange of ions, the latter consists in an exchange of cations between the solution and the solid phase and the exchange is in gram-equivalent quantities. Since the reactions in the zeolitic portion are of a surface character it is understood that the degree of dispersion of the particles has an important bearing, especially in the alkali soil where the colloidal content is high. And from this angle the study of the behavior of the alkali soil extract is of extreme interest.

The theories advanced by Gedroiz seem quite logical and some of our experimental data seem to verify the course of reactions outlined. Still there is this to be said: First, we have to agree to the fundamental assumption of the zeolites in the soil. Second, there is the possibility of reactions as given by Hilgard; stoichiometric considerations of concentrated solutions of sodium salts and calcium carbonates admit the postulate of reactions between these compounds and the formation of soda in soils. And besides the zeolitic sodium as it is forced out from the complex may easily unite with the CO_2 of the soil air forming Na_2CO_3.

The earlier work of Gedroiz has been reviewed by Cummins and Kelley (2). They do not mention his recent paper(8) in which he shows that the absorption of cations in the zeolitic portion is of a physico-chemical nature. There is an actual replacement in the silicate complex at the surface or surface layer. The degree of dispersion of the particles plays its part inasmuch as the total surface is affected by it. The theory of Dominicis (3) as pointed out by Cummins and Kelley is similar to that of Gedroiz. Dominicis assumes that the hydrogels formed by a replacement process in certain silicates and humate combinations change into hydrosols. Dissociation of the sodium takes place and the formation of sodium hydroxide which absorbs CO_2 and forms sodium carbonate. In this respect he differs with Gedroiz, since the latter distinctly shows that the presence of $CaCO_3$ is essential for the formation of soda. The work of Cummins and Kelley (2) seems to substantiate the hypothesis of Dominicis, since water percolates of soil treated with NaCl solution gave a strongly alkaline reaction, even though they contained no calcium carbonate. They show that the sodium fixed is an exponential function of the concentration of the sodium salt remaining in solution at equilibrium; also that the combined Ca, Mg and K passing into solution are chemically equivalent to the sodium fixed. They also point out that soluble calcium salts when present in sufficient concentration prevented the formation of hydrolyzable silica com-

pounds in the soil. Undoubtedly this is due to the coagulation effect of the calcium.

Cummins and Kelley in their interpretation of the chemistry of alkalinity approach the theories advanced by Gedroiz; it is unfortunate that the splendid work of this investigator is in obscurity, on account of the inaccessibility to the Russian. If Cummins and Kelley (2, p. 27) would appreciate more fully the theories of Gedroiz they could easily explain "how a soil can yield a percolate containing 3 per cent sodium carbonate, for instance, and yet contain no determinable amount of residual alkalinity." The coefficient of adsorption of the hydrogen ion is great and replaces the sodium which gives the soda; the residual condition is an unsaturated one, i.e., the hydrogen ion from the water is taking the place of the sodium in the alumino-silicate complex. The replacement process has been completed, i.e. all the zeolitic cations capable of replacement have been forced out by the percolation process.

Whether the theory of Gedroiz is upheld or that of Dominicis as supported by the researches of Cummins and Kelley (2) the fundamental question in the amelioration of alkali soils is to replace the sodium in the silicate complex (theory of Gedroiz) coagulating the colloids (theory of Dominicis) and eventually leach out the excess of soluble salts. For these operations any cation with a high energy of absorption will accomplish the task. The efficiency of adding gypsum, alum or sulfur is to be looked upon from the standpoint of their relative power to accomplish the reactions pointed out. The gypsum on account of its slow solubility is not an active ingredient, although the flocculating effect is quite marked and the replacement of calcium will take place in the silicate. Hibbard (10) leached alkali soils with a water solution of gypsum. He showed that on account of the low solubility of gypsum it was possible to add only 10 per cent of the gypsum calculated necessary to neutralize the alkalinity.

From the viewpoint of the mass laws equation, the reaction between $CaSO_4$ and Na_2CO_3 shows that there is always the tendency to form Na_2CO_3 again:

$$Na_2CO_3 + CaSO_4 \rightleftarrows Na_2SO_4 + CaCO_3$$
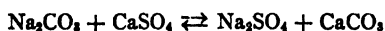
If the gypsum should react with the carbonates in solution without the reversible effect, the formation of $CaCO_3$ would tend to form more Na_2CO_3 later, bringing out some of the sodium from the zeolitic portion as Gedroiz wants it or the "absorbates" as Dominicis calls it. Lucas (20) in discussing the general origin of sodium carbonate in nature gives several possible reactions and one of them is the reaction between salts and zeolites and kindred compounds. Mondesir (21) exhibited to the Academie des Sciences 100 gm. of Na_2CO_3 which he had been able to produce by treating one kilogram of soil with sodium salts and, then leaching with water. He appreciated the base exchange in soils; unfortunately his theory of formation of Na_2CO_3 has been overlooked. Prescott (22) shows how some of the Egyptian soils when treated with sodium

salts replace Ca and Mg and upon leaching bring out from the complex (the zeolitic portion as it is called by Gedoriz) Na ions and in the presence of CO_2 sodium carbonate is actually formed.

Kelley and Thomas (15) report experiments with sulfur on black alkali soils with various proportions of water soluble salts. They found that calcium was made soluble after all of the carbonates had disappeared. The carbonates and bicarbonates are simultaneously attacked by the acid formed. They seem to think that black alkali soils must be regarded as being sodium saturated soils. Scofield and Headley (25) in a study on the physical condition of soils in relation to the alkali problem present data showing that neutral sodium salts produce among other things a strongly alkaline reaction. They neglected to discuss the possibility that such treatment is responsible for the exchange of bases in the zeolitic portion of the soil.

From what has been said it is fair to conclude that any rational system of alkali soil treatment has to take into consideration the following principles: (1) coagulation of the colloids, (2) washing out excess of soluble salts, (3) replacement of the zeolitic cations, (4) creating a reaction favorable for plant growth, and (5) compensating the loss of plant food caused by the methods of amelioration.

The experiments reported in this paper were started in order to determine whether the biochemical oxidation of sulfur (12, 13, 18) which takes place even in alkali soils (although the organisms involved in the oxidation of sulfur do not grow in artificial culture media at the reaction of alkali soils) may be utilized in reclaiming alkali soils.

The first two points have been discussed in the first paper; some features of the second point and the others are the subject of discussion of the following papers.

Empirically some approach to treat alkali soils as just outlined has been made. Gypsum with all its drawbacks, as pointed out, does in some way accomplish a coagulation of colloids and replaces the zeolitic sodium. The permeability of alkali soils improved by the addition of gypsum allows leaching operations. At this point it is of interest to look into the chemical effects of water, provided conditions are favorable for leaching. It is known that the reaction power of any soil solution is determined by the concentration of hydrogen ions. Although pure water does not dissociate very much, there are some free hydrogen ions [dissociation constant of water = $Kw = 1.1 \times 10^{-14}$, as determined by Kohlrausch and taken from Clark (1)]. True enough, the concentration is very small but in the case of leaching the bulk of water may give a total concentration of hydrogen ions which may be of considerable moment. Moreover, the dissociation constant of water is increased if ionizable salts are present in solution. From theoretical considerations prolonged leachings with water ought to accomplish the same effect as with an acidified solution or with some neutral salt with a cation of high energy absorption. In practice, however, leachings operations are impossible due to the fact that the

colloids present produce a spongy effect and prevent the permeability of water. Furthermore, if the zeolitic portion is saturated with sodium, the replacement of hydrogen ions brings about a more alkaline condition and this in turn decreases the permeability. In the case of gypsum the slightly favorable effects on coagulation of the colloids and permeability of the soil are quickly counteracted by leaching. The sodium carbonates formed due to the replacement of the sodium in the zeolites serve as a strong peptizing agent and the original condition is brought about again.

The effects of alum as suggested by Scofield (23) will be discussed more fully when the experimental results are reported.

The soil investigated was obtained from the California Experiment Station, Riverside, California. Originally the soil came from Fresno. In texture it is a sandy loam, strongly alkaline with a pronounced soda odor, having a pH reading varying from 9.6 to 8.8 depending chiefly on the increase or decrease of the carbonates and bicarbonates. The data on the amount of carbonates and bicarbonates in the untreated cultures at various periods of incubation show the fluctuations. This indicates a displacement of equilibrium between the carbonates and bicarbonates. The conditions affecting this equilibrium are concentration, temperature and other side reactions. The activity of such changes is expressed by the speed it proceeds. The general principle covering such changes is known as the *law of molecular concentration:* "In any given chemical change the apparent activity and therefore the speed of that change is proportional to the molecular concentration of each of the interacting substances." Due to the change in concentration of the carbonates and bicarbonates the amount of them even in the untreated soils is not constant. At the start the amount of carbonates was about 500 pounds per acre calculated as Na_2CO_3. At times it ran up as high as 600 to 700 pounds and as low as 300 pounds. The variations in the bicarbonate content are governed by the carbonates. At the start the bicarbonates were up to about 6000 pounds, calculated as $NaHCO_3$. The chlorine content of these soils runs up to 8000 pounds per acre on the basis of two million pounds of soil per acre.

In the first series of experiments, flower pots of 1.4-pound capacity were used to study the effects of the various treatments on leaching. Earthenware glazed pots of 16-pound capacity were used for the study of the effects of various treatments without leaching. In order to prevent absorption by the clay walls of the flower pots the latter were boiled for 15–20 minutes in paraffin. It was found later that this treatment was not enough to prevent absorption. Besides, fungi developed on the paraffin. All of that introduced complications which will be pointed out presently. Moisture was added equal to 60 per cent of the total moisture-holding capacity. The pots were kept in the greenhouse and were thus subject to constant variations in temperature which undoubtedly had its effects on the displacement of equilibrium spoken of above.

In the second series of experiments which followed the first series some slight modifications were made. The pots used were earthenware glazed pots of 3 pounds capacity with holes on the bottom for leaching. Some of the pots received sulfur mixed in with the surface four inches of soil, others were mixed with the bulk of soil. The idea of applying the sulfur to the surface four inches was to see whether diffusion would effect the desired changes; this would also indicate the possible effects of sulfur oxidation on the subsurface soil.

TABLE 1

Treatment of alkali soils

NUMBER	TREATMENT	
	First series	Second series
1	None	None
2	4000 pounds sulfur	2000 pounds sulfur*
3	4000 pounds sulfur, 5 tons peat	2000 pounds sulfur†
4	6000 pounds sulfur	4000 pounds sulfur*
5	6000 pounds sulfur, 5 tons peat	4000 pounds sulfur†
6	2000 pounds sulfur	6000 pounds sulfur*
7	2000 pounds sulfur, 5 tons peat	6000 pounds sulfur†
8	4000 c.p. alum, 5 tons peat	4000 pounds c.p. alum
9	4000 c.p. alum, 2000 pounds sulfur	
11	5 tons peat	

* Sulfur was applied to surface 4 inches.
† Sulfur was mixed with bulk of soil.

TABLE 2

Rate of sulfur oxidation

TREATMENT	INCUBATION PERIOD			
	14 days	60 days	95 days	140 days
	Sulfur oxidized			
	per cent	*per cent*	*per cent*	*per cent*
2000 pounds sulfur..........................	34	60	87	71
4000 pounds sulfur..........................	20.9	37	60	55
6000 pounds sulfur..........................	17	26	57	52

Other features of the second series will be pointed out as the results are discussed. The second series of pots were kept at room temperature.

Table 1 gives the scheme of treatments of both series.

We shall take up separately the physical, chemical and biological effects of the various treatments. The rate of sulfur oxidation bears directly upon these effects. Accordingly, a record of the sulfur oxidized at the various incubation periods of the first series is presented in table 2.

The significance of the rate of oxidation of sulfur will be taken up later; at this point we shall interpret the effect of the sulfuric acid produced from the oxidation of sulfur on the physical condition of the soil.

EFFECTS ON THE PHYSICAL STRUCTURE

After twenty-four hours, 1 pound of soil was removed from the large pots (first series), air-dried and placed into glass tubes (¾ inch inside diameter, 4 feet long) and compacted by pounding gently on a rubber block. Fifty cubic centimeter of tap water was poured upon the top of the column in each tube. After twenty-four hours of contact with the water, the length of the column penetrated by the water was measured and it was found that the alum treated soils were quite permeable; all of the water was absorbed and none was standing on the surface. In all other tubes the water was still on the surface and the length of column penetrated was only 5–6 inches against the 15 inches in the alum-treated soils. It is evident that the alum coagulated the colloids and as a result negative adsorption increased and the permeability improved. The same effect of the alum may be noticed from figure 1 which gives the curves on the capillary rise of water after 14 days' incubation. The alum treatment exerted a beneficial effect on the permeability of the soil. However, as the period of incubation was prolonged, the beneficial effects of the alum treatment gradually disappeared. This is brought out in figures 2, 3, 4, 5, 6.

The curves of the figures represent the two series of experiments as outlined in table 1. The general tendency of the curves is the same in both series: The alum treatment is not permanent, not even lasting, while the sulfur treatment shows progressive improvement as the period of incubation is prolonged. There are, however, other features which deserve special attention and for that reason it is important to consider the two series of curves separately. Figures 1–4 are the curves from the first series. It has been noted already (14) that the cultures treated with alum after 14 days as shown in figure 1 have a total rise greater than any other. This indicates that the strongly adsorbed trivalent aluminum ion exerted its influence by coagulating the colloids and thereby decreasing the surface increasing negative adsorption and thus improving the permeability. As the period of incubation was prolonged the effect of the alum gradually disappeared. After sixty days, as may be seen from figure 2, there is a wide difference of capillary movement between culture no. 8 (treated with alum) and the cultures treated with sulfur. The same is true after 95 days and 140 days as shown in figures 3 and 4. Attention should be called at this point to the reaction of the extracts of culture 8 (treated with alum) at the various incubation periods. It is instructive to learn that after 14 days the pH of culture 8 was 8.2, and after 60 days, it was 8.6. After 140 days we find some carbonates in culture 8 showing that the pH reading is not lower than 8.2.
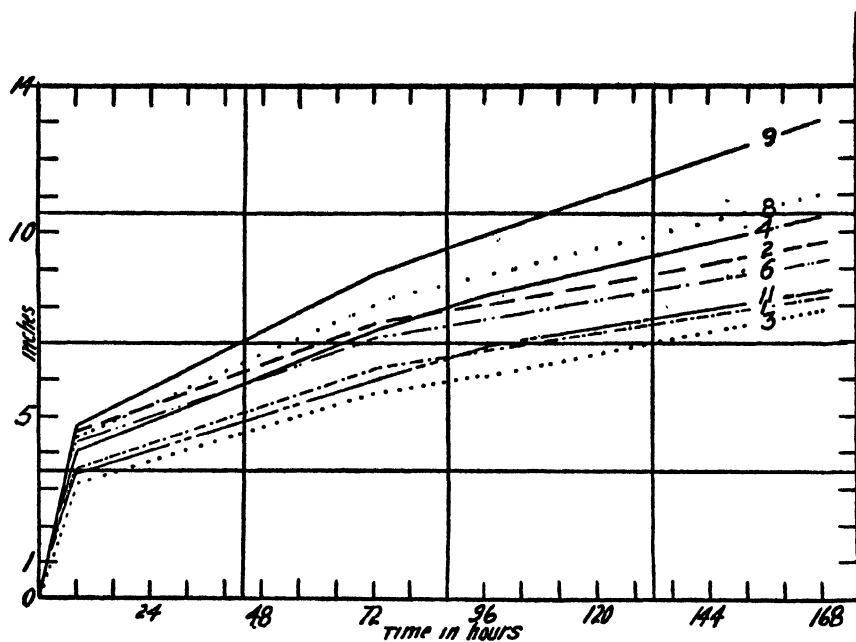
FIG. 1. RISE OF CAPILLARY WATER IN UNLEACHED SOILS OF THE FIRST SERIES OF EXPERIMENTS AFTER 14 DAYS INCUBATION
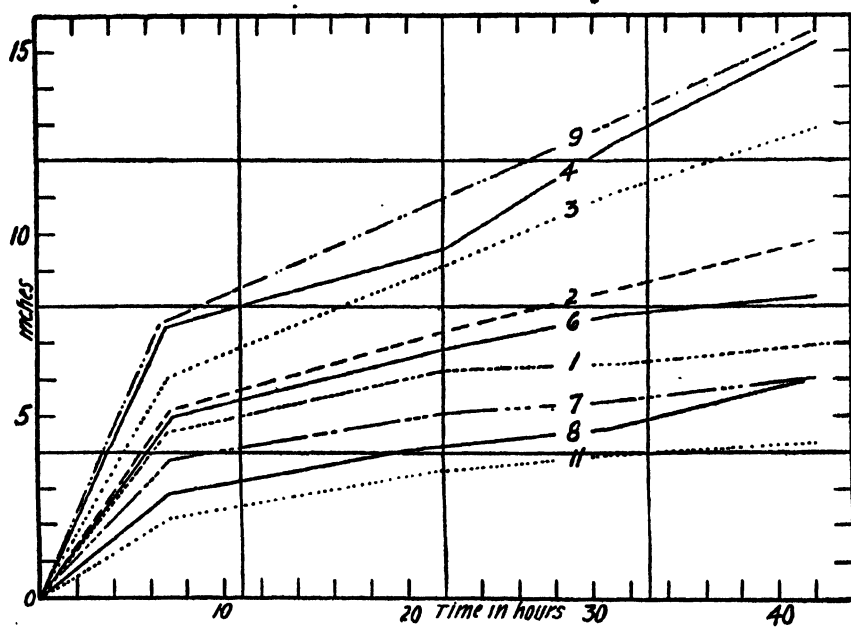
FIG. 2. RISE OF CAPILLARY WATER IN UNLEACHED SOILS OF THE FIRST SERIES OF EXPERIMENTS AFTER 60 DAYS INCUBATION
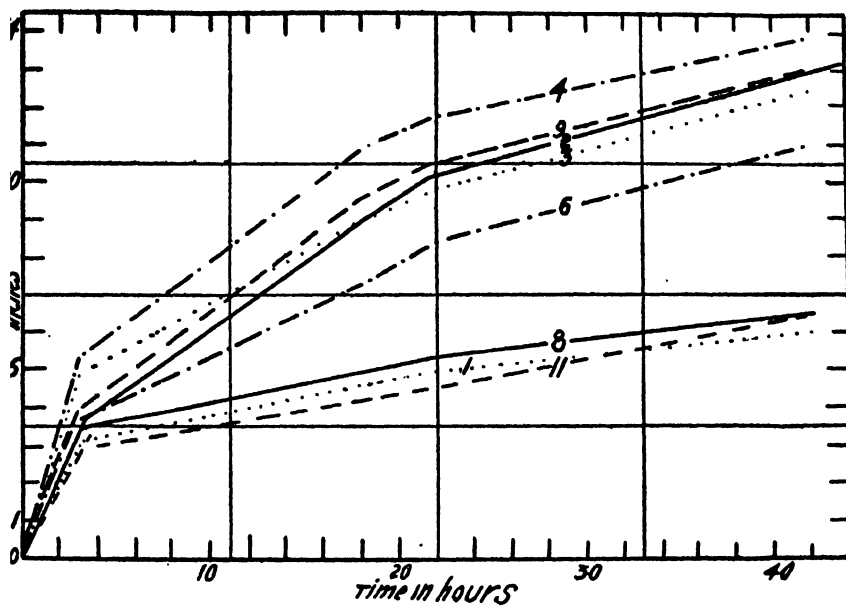
FIG. 3. RISE OF CAPILLARY WATER IN ALKALI SOILS OF FIRST SERIES AFTER 95 DAYS INCUBATION
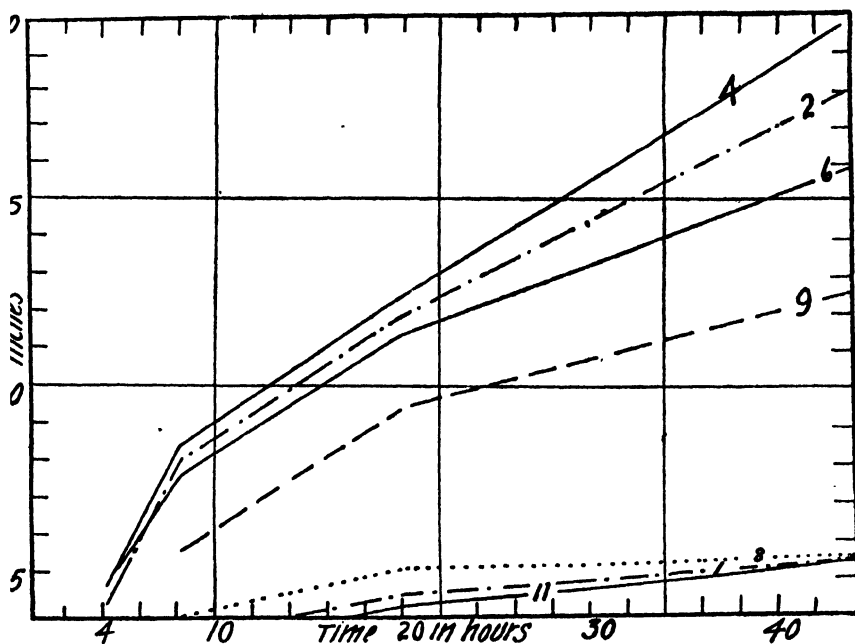
FIG. 4. RISE OF CAPILLARY WATER IN UNLEACHED ALKALI SOILS OF THE FIRST SERIES OF EXPERIMENTS AFTER 140 DAYS INCUBATION
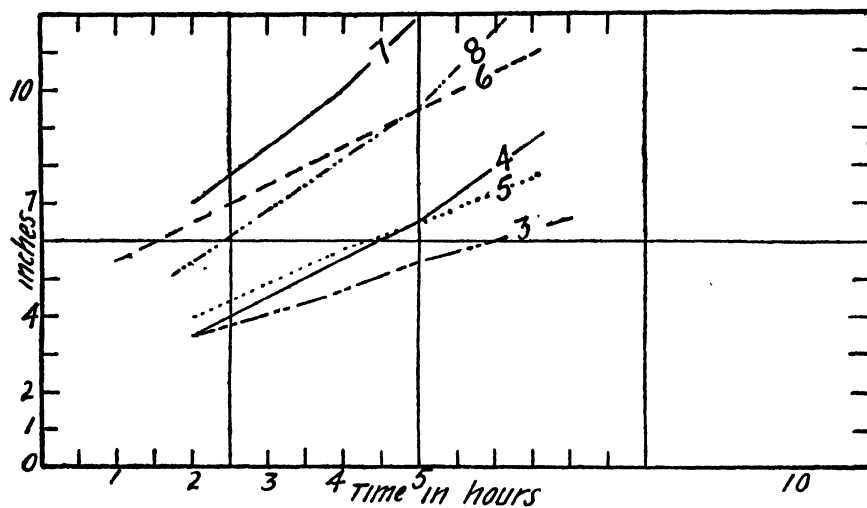
FIG. 5. RISE OF CAPILLARY WATER IN LEACHED ALKALI SOILS OF THE SECOND SERIES OF EXPERIMENTS AFTER 30 DAYS INCUBATION
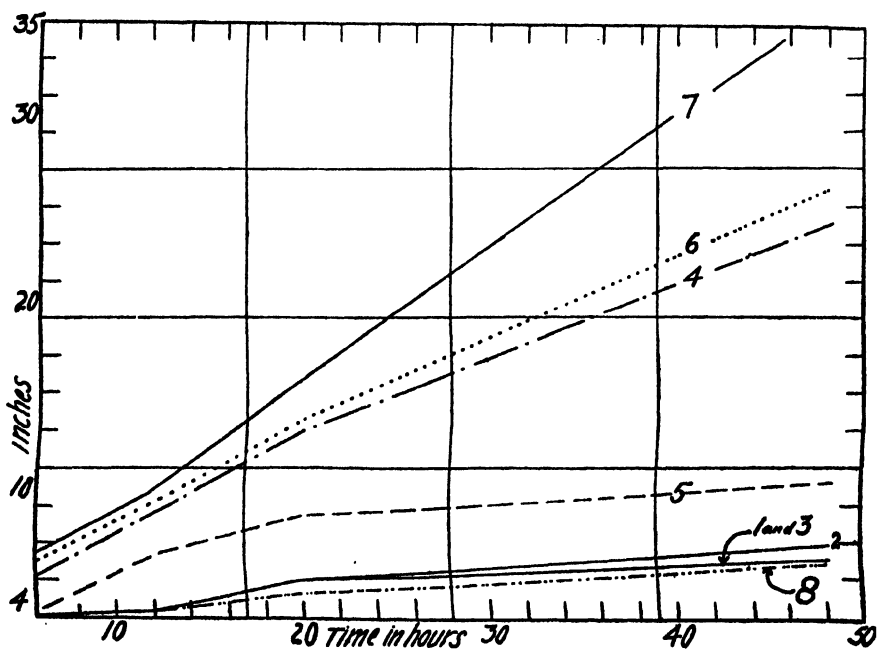
FIG. 6. RISE OF CAPILLARY WATER IN LEACHED ALKALI SOILS OF THE SECOND SERIES OF EXPERIMENTS AFTER 75 DAYS INCUBATION
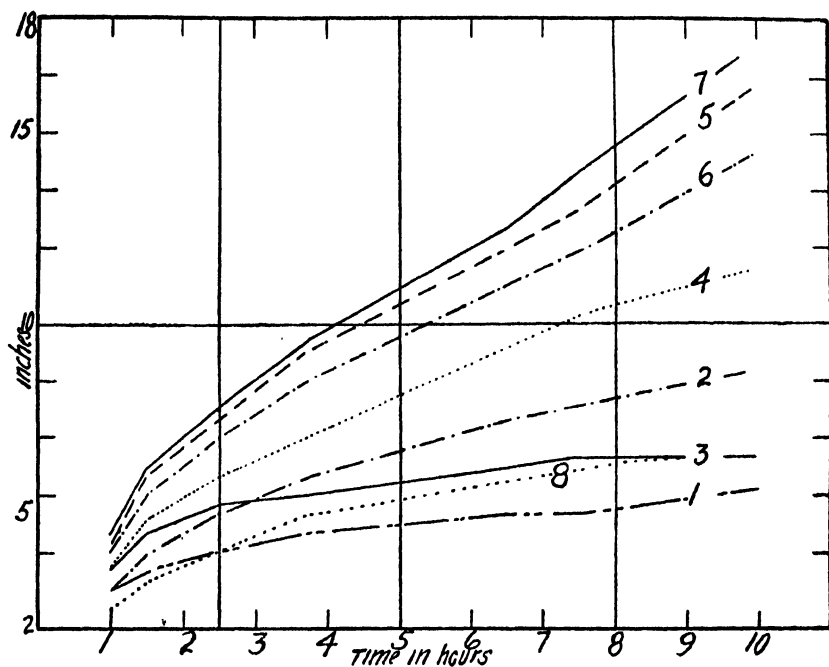
FIG. 7. RISE OF CAPILLARY WATER IN LEACHED ALKALI SOILS OF THE SECOND SERIES
AFTER 140 DAYS INCUBATION
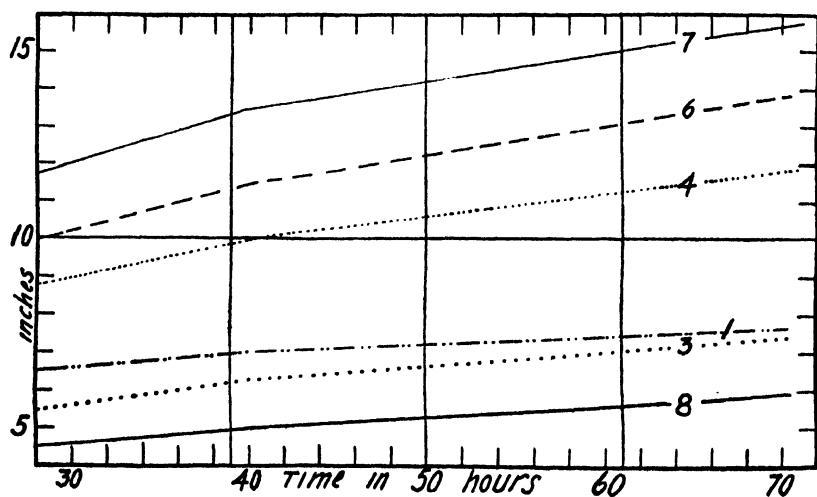
FIG. 8. RISE OF CAPILLARY WATER IN UNLEACHED ALKALI SOILS OF THE SECOND SERIES
OF EXPERIMENTS AFTER 190 DAYS INCUBATION

Examining the curves of the second series of experiments (fig. 5–8) we note the same phenomenon. The alum treatment improves the soil temporarily but the alkalinity is returning after a short time. From considerations of practicability alum may be used as a temporary ameliorating agent. Wherever a single leaching will wash out the soluble salts and bring the soil back to productiveness it should be advisable to coagulate the colloids and improve the permeability by additions of alum. In general, however, such a temporary relief is not to be considered in a rational scheme of treating alkali soils.

On the basis of the flocculating power of aluminum, Scofield (24) suggested the use of aluminum salts as a treatment for certain badly deflocculated soils of the semi-arid regions. He points out that at the rate of 10 tons per acre (he does not state the percentage purity of the alum used) a very marked change has been shown in the physical condition of the soil. How long the effects lasted has not been given. Kelley and Thomas (15) in their experiments with alum (ordinary potassium alum was used) find that the addition of alum reduced the alkalinity effectively. Their procedure was to mix the dry alum salt with the soil and the mixture was extracted with water. They recognize the fact that alum solutions are acidic in nature (0.01 M c.p. alum used in our experiments gave a pH reading of 3.0) and of course some of the alkali carbonates have been neutralized. They did not, however, leave the mixture in contact for a long period of time to see what would happen. Undoubtedly the alkalinity would have appeared again as it happened in our experiments. The chemistry of the process may be pictured as follows: the alum is coagulating the colloids and hydrous aluminum oxide is precipitated; this sets free some of the sulfate anions which combine with the sodium from the carbonates and bicarbonates as indicated in the equation:

$$Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24\ H_2O + 6\ NaHCO_3 \rightarrow$$

$$K_2SO_4 + 3\ Na_2SO_4 + 2\ Al(OH)_3 + 6\ CO_2 + 24\ H_2O$$
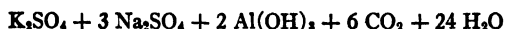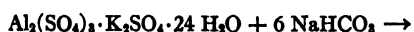
It is obvious that the CO_2 formed combines readily with some of the sodium replaced from the zeolites as soon as the Na_2SO_4 is leached out. Even without leaching there is a chance for some of the hydrogen ions, which have a high coefficient of adsorption and also some of the Al ions to replace sodium and other cations. The result is augmentation and accumulation of Na_2CO_3. The presence of Na_2CO_3 under such conditions will react with the precipitate $Al(OH)_3$ and give the well known "neutral alum," a basic salt $K_2SO_4 \cdot Al_4(OH)_6 \cdot (SO_4)_3$. From this we may get again a precipitation of the aluminum hydroxide if an acid reaction is maintained in the system. Otherwise the ameliorating effect is lost. The side reactions such as the replacement of Ca and Mg, of which we must be aware, will not alter much the general scheme of reactions outlined. That an acid reaction, or better to say a less alkaline reaction, is favoring the desirable physical improvements in alkali soils may be well illustrated in figures 1–4 by the curve no. 9, representing the treatment of

alum and sulfur. It will be noticed that the combined alum and sulfur treatment had a very beneficial effect on the capillary movement of water which serves as an index of the improvement in the physical condition of the soil. After fourteen days, as may be seen from figure 1, the combined alum and sulfur treatment shows its superiority over any of the treatments. The same is true after sixty days, although at this time the alum alone has ceased to exert its influence and the curve runs even lower than the control. There is one question however which suggests itself: "Why does curve no. 9 show a greater capillary rise than curve no. 6, which has 2000 pounds of sulfur, an amount similar to no. 9?" Judging from no. 8, the alum should have no more effect at this time; however, it is superior in its effects even over no. 4, the highest sulfur application. A little insight into the possible reactions will clear up the apparent discrepancy. As pointed out above an acid reaction tends to keep up the efficiency of the alum and this is what happens in no. 9. The oxidation of sulfur produces sulfuric acid and as the Na_2CO_3 is formed it is partly attacked by the H_2SO_4 formed. Besides, the excess of SO_4 anions prevents the replaced sodium cations from the zeolites to combine with the CO_2; this may easily be explained on the basis of the mass law effect. As the period of incubation advances the combined alum and sulfur effect is waning and at 140 days we find (fig. 4) that no. 9 is even below no. 6. This would indicate that even under conditions of less alkalinity the favorable influences of alum eventually dwindle. It is very probable that the aluminum as a trivalent ion has a high coefficient of adsorption and replaces more sodium and other cations from the zeolites. These combine with the sulfates, silicates, etc., hydrolyze and again turn into colloidal state. This precludes the conclusion that as long as there are replaceable cations in the zeolitic portion any ameliorating agent will fail. The problem thus resolves itself to determine quantitatively the amount of zeolitic cations subject to replacement. This subject is now under investigation.

Notice should be taken of the favorable effects of the higher amounts of sulfur treatment. It is apparent that the quantity of hydrogen ions of the sulfuric acid formed is thus far sufficient to replace the cations in the zeolites and check the formation of the Na_2CO_3 by increasing the SO_4 component in the system and thus forcing the formation of the neutral sulfate, thereby retaining the favorable physical effects.

No mention was made of the effect of peat, either by itself or in combination with sulfur, or with alum. The data on hand does not warrant any conclusion. None of the peat treatments showed any outstanding results and from the standpoint of physical improvement the experiments showed no visible effects.

Figures 5–8 give the curves of the second series of experiments. It is well to recall that in this series diffusion effects were to be studied. For that purpose sulfur was mixed with the top four inches of soil in some of the cultures. The peat treatment was also omitted in this series. An analysis of the curves shows that the general tendency is for the higher sulfur treatments to lead in

efficiency of physical improvement. The alum again shows that at the time of application it improves the condition but the efficiency gradually goes down to zero and even becomes negative. Attention is called to the fact that the curves of this series, except no. 8 (190 days), represent capillary movement of water after leaching. The soils were leached with 400 cc. of water, air-dried and placed in the tubes as outlined previously. Some interesting features may be demonstrated. First of all the leachings exert an unfavorable effect on the lower sulfur applications. Apparently after washing out the accumulated sulfates more of the cations from the zeolites go into solution forming more carbonates. After that time there is not enough sulfuric acid formed to prevent the sodium to form carbonates which wipe out the improvements produced. The alum treatment after 30 days' incubation and after leaching showed itself on par with the cultures which received the highest amount of sulfur in respect of capillary movement. In the light of the reactions of aluminum and carbonates as outlined above it may well be explained why just at the start the physical condition is improved. As the period of incubation is advanced more cations are replaced, they unite with the CO_2, appear in solution and introduce an alkaline reaction. This is borne out by the data on the reaction of the extracts as shown in the next paper.

In reference to the diffusion effects of the sulfuric acid formed from the oxidation of sulfur it may be seen from the curves that a surface incorporation of sulfur is not as effective as mixing the sulfur with the bulk of soil. However, the acid is diffusing and, since such a surface incorporation is more closely comparable to field conditions, it is fair to infer that such action will take place in the field, provided environmental conditions for sulfur oxidation are favorable.

Another expression of the physical effects brought about by the various treatment is the amount of leachings as shown in table 3.

The leaching operations were conducted as follows: 400 cc. of water[3] were applied to the surface of the pot; in the first two samplings of the first series (after 14 and 48 days) the time of contact of water with the alkali soil was not limited. All treatments were leached through in about the same period of time. Later on the control cultures and the alum treatments began to fall behind and even after seven days not all the water had leached through. For that reason the water was kept in contact with the soil only 48 to 72 hours after which time it was poured off. It will be noticed that in the first series the amount of leachings in the alum treatment follows closely the course of the capillary movement of water. The alum introduces a temporary effect which is gradually disappearing. Some inconsistencies that may be pointed out are undoubtedly due to the absorbing effects of the clay pots on account of the inefficiency of paraffining. In general, however, the tendency is well defined. The data on

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[3] Tap water was used in the first series; distilled water, in the second because of the variability in the tap water. The same kinds of water were used for making up the evaporation losses in either series.

the leaching in the second series are not so outstanding. The physical improvement brought about by the alum is persisting a longer period. However, at 190 days we notice the decline of the alum treatment and leaching operations made after 8, 9, 10 and 11 months showed that the alum treatment has no more effect. It is very likely that the difference in the water applied (distilled in the second series) and the environmental condition of incubation (first series in greenhouse, second series at room temperature) made the difference in the effectiveness of the alum treatment. At any rate the physical effects of the alum and especially of alum and sulfur are significant and more work is contemplated in this direction.

In the next paper the chemical effects of the treatments will be taken up.

TABLE 3

Leachings obtained at various incubation periods from alkali soil cultures differently treated

LABORATORY NUMBER OF TREATMENT	FIRST SERIES				SECOND SERIES			
	14 days	48 days	95 days	140 days	30 days	75 days	140 days	190 days
	cc.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
1	188	102	75	20	165	105	150	60
2	168	260	285	210	180	205	230	252
3	160	125	298	205	153	155	225	225
4	159	262	290	195	224	250	237	215
5	195	312	293	205	182	190	255	270
6	182	158	90	110	212	270	260	250
7	175	142	150	205	127	240	237	220
8	180	230	138	145	200	230	225	125
9	225	265	210	65				
11		78	53	10				

SUMMARY

The theory of base exchange is the corner stone of the research on the origin of alkali soils. The contributions of Gedroiz were considered in some detail because of the important theories advanced by him. A brief review of the work done at the California Agricultural Experiment Station and others has been given.

The problem of alkali soil treatment has been presented and the chief points involved outlined.

Experimental work reported includes an outline of the methods used in treating the alkali soils and a discussion of the effects, with special reference to the physical structure of the alkali soils.

A series of eight curves illustrates the capillary movement of water in alkali soils variously treated.

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SOME CHANGES BROUGHT ABOUT IN CYLINDER SOILS BY LONG CONTINUED CROP AND FERTILIZER TREATMENT[1]

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The chemical composition of the soil is constantly changing, but our present methods of analysis are not delicate enough to enable us to detect certain of these changes, unless the determinations be made to cover periods of several years. It is important, however, that such determinations should be made, for otherwise it is difficult to tell whether a given system of agriculture is one of soil building or of soil robbery.

It may be argued that the crop yields should answer this question. Unfortunately they frequently do not until it is too late to help the individual farmer. The changes take place so slowly that the yields may run along about uniform, fluctuating according to weather conditions, with little indication of decline, while the reserve supply of plant food (in the case of nitrogen and organic matter especially, the accumulated wealth of centuries) is being gradually eaten up. At last, after a period of fifteen to twenty-five or fifty years, the breaking point comes and the land no longer yields its accustomed averages. Crop failures are more frequent and finally a certain proportion of once prosperous farm lands is abandoned, or left to tenants and foreigners who have little knowledge of the potential productive capacity of the land and less ambition for the creating of a united farm community.

Thousands of·soil analyses are on record, but aside from the records at the Rothamsted Experimental Station there are apparently few instances where it is possible to compare the analysis of the original soil with the analysis of the same soil after twenty or twenty-five years of crop and fertilizer treatment.

In this connection Gilbert (5) reports some figures which are of interest and throw some light on the subject of soil depletion. Three Rothamsted arable soils which had been under experimental observation, in the growing of root and grain crops, for thirty to forty years gave an average of 0.108 per cent nitrogen; seven rich Russian soils an average of 0.341 per cent nitrogen and eleven United States and Canadian prairie soils 0.340 per cent nitrogen. Thus it will be noted that the Rothamsted soils, which have probably been under cultivation for several centuries, contain less than one-third of the nitrogen found in the American prairie and rich Russian soils.

In discussing the character of a rich virgin soil Gilbert (5) says: "But not only the facts obtained in our own and other investigations, but the history of agriculture throughout the

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world, so far as we know, clearly shows that a fertile soil is one which has accumulated within it a residue of ages of previous vegetation, and that it becomes infertile as this residue is exhausted; and enormous as are the accumulations in the prairie lands of the American continent it is still desirable to postpone, rather than to accelerate, the time of their exhaustion."

The soil used in the cylinder experiments which were started at the New Jersey Station in 1898 provides an excellent opportunity for a study of this problem. This experiment has been described in earlier papers (9, 16) and only brief reference need be made to it here. The soil is that described by the Bureau of Soils as Penn Loam (2), derived from the Triassic red shale.

The work was originally outlined under the rather broad heading, "Investigations relative to the use of nitrogenous fertilizer materials." The plan included a careful study of nitrogen availability, and other phases of the nitrogen problem. A five-year rotation has been carried out and this together with the fertilizer and manure treatment have brought about certain very definite modifications in the composition of the soil. Nitrogen has been applied annually throughout the period in the form of nitrate of soda, sulfate of ammonia, dried blood and cow manure. The manure has been used at the rate of approximately 16 tons per acre annually (4 gm. nitrogen per cylinder), both alone and in combination with the commercial materials. Nitrate of soda has been used at the rate of 160 and 320 pounds per acre, and sulfate of ammonia and dried blood in amounts per acre equivalent to the 320 pounds of nitrate of soda.

The arrangement of the cylinders in the experiment is shown in figure 1. All cylinders except the three of series 1 have received annual applications of acid phosphate at the rate of 640 pounds, and muriate of potash at the rate of 320 pounds per acre. When the soil was first prepared, a liberal application of lime, in the carbonate form, was made for all cylinders, but no further lime treatment was given for the first ten years. In 1908—beginning the third five-year period—lime was again applied to the B and C cylinders of all the series, but none was applied to the A cylinders. This lime treatment (at the rate of two tons per acre) for the B and C cylinders has been repeated at intervals of five years. The plan of applying manure and fertilizers is indicated in figure 1, reference to which has already been made.

Careful records have been kept of the crops grown on these cylinders throughout the period, and nitrogen determinations have been made for all the crops. It is possible, therefore, to calculate the amount of nitrogen applied to all of the cylinders and the amount removed by the crops. Phosphoric acid and potash have also been determined in representative samples of each crop, but these constituents have not been determined in all samples of the different crops.

Determinations have been made of the total nitrogen, phosphoric acid, potash, lime, magnesia and carbon in the original soil and of total nitrogen, phosphoric acid, lime and carbon in all of the sixty cylinder soils, and potash,

Series

1. Check.

2. Minerals (20 gm. acid phosphate and 10 gm. muriate of potash).

3. Minerals, manure, solid, fresh.

4. Minerals, manure, solid and liquid, fresh.

5. Minerals, manure, solid, leached.

6. Minerals, manure, solid and liquid, leached.

7. Minerals, nitrate of soda, 5 gm.

8. Minerals, nitrate of soda, 10 gm.

9. Minerals, manure, solid, fresh; nitrate, 5 gm.

10. Minerals, manure, solid, fresh; nitrate, 10 gm.

11. Minerals, manure, solid and liquid, fresh; nitrate, 5 gm

12. Minerals, manure, solid and liquid, fresh; nitrate, 10 gm.

13. Minerals, manure, solid, leached; nitrate, 5 gm.

14. Minerals, manure, solid, leached; nitrate, 10 gm.

15. Minerals, manure, solid and liquid leached; nitrate, 5 gm.

16. Minerals, manure, solid and liquid leached; nitrate, 10 gm.

17. Minerals, sulfate of ammonia, equivalent to 10 gm. nitrate.

18. Minerals, dried blood, equivalent to 10 gm. nitrate.

19. Minerals, manure, solid leached; sulfate of ammonia as in 17.

20. Minerals, manure, solid, leached; dried blood as in 18.

FIG. 1. DIAGRAM OF EXPERIMENT

magnesia and manganese in certain samples, which are regarded as representative of the entire lot.   Determinations made on the original soil gave the following results:

		per cent
Phosphoric acid	...	0.225
Potash	...	2.634
Lime	...	0.807
Magnesia	...	2.241
Total nitrogen	...	0.197
Total carbon	...	1.825

Since the nitrogen balance of these soils has been fully discussed in earlier papers (9, 10) it is not deemed necessary to repeat that part of the discussion. It may be added that the records for the first ten years show an average annual loss of nitrogen, exclusive of that removed by crops, of 103 pounds per acre. For the fourth five-year period the average loss was considerably reduced, and for certain of the A and C cylinders there was some gain.   The gain on the C cylinders should no doubt be attributed to symbiotic fixation through legume cover crops which were grown on these cylinders twice during each five-year period.   It is pointed out that with continuous cultivation it is exceedingly difficult to maintain a high nitrogen content of the soil, except at wasteful expenditure of nitrogenous fertilizers.

In addition to the removal of nitrogen by crops there is the constant dissipation and loss of nitrogen through the decomposition of organic matter.   The more intensive the cultivation and the higher the rate of fertilizing the greater is the loss.

In discussing the analysis of Rothamsted soils in his report on "Fertility" in 1881, Sir John B. Lawes (8) says: "With regard to the nitrogen in the soil each analysis shows a reduction in the amount present as compared with that which preceded it.   The difficulty consists in fixing the actual amount of such reduction.   I am disposed, however, to estimate it at from 1000 to 1200 pounds per acre during the forty years, which would be considerably more than the amount of nitrogen carried off in the crops of wheat."

Lawes sums up his discussion on this point as follows: "We have evidence of a very large loss in the accumulated stock of nitrogen, based upon the assumption that my land was originally pasture; there is a further large loss during the period in which the land has been under experiment and growing unmanured corn crops.   The crops are declining; the amount of nitrogen removed each year in the crops is declining; and, therefore, a considerable reduction of the nitrogen in the first 9 inches, with an indication of a small reduction in the second 9 inches, is shown by different analyses of the soil itself."

The much larger annual loss of nitrogen from our cylinder soils than from the Rothamsted soils would appear to be due to the very liberal use of manure and nitrogenous fertilizers, and to the heavy cropping.

TOTAL PHOSPHORIC ACID (P_2O_5) IN SOILS AND CROPS

The percentages of phosphoric acid in the soil representing the individual cylinders are shown in table 1.   Comparing these figures with the percentage in the original soil (0.225 per cent) it will be observed that there has been an

increase in phosphoric acid content for all the cylinders except the three of series 1, where no phosphoric acid has been applied during the twenty-five years. In the soils of this series there has been a slight loss, though less than would be expected under the existing conditions. It must be borne in mind, however, that the crops on these cylinders have been small, no fertilizer of any kind having been applied.

TABLE 1

Per cent total phosphoric acid (P_2O_5) in cylinder soils after twenty-five years cropping
(sampled in 1922)

SERIES		CYLINDER A	CYLINDER B	CYLINDER C
		per cent	*per cent*	*per cent*
1	Check.................................	0.181	0.169	0.194
2	Minerals...............................	0.237	0.242	0.283
3	Minerals, manure, solid, fresh...............	0.333	0.320	0.372
4	Minerals, manure, solid and liquid, fresh......	0.369	0.288	0.341
5	Minerals, manure, solid, leached.............	0.335	0.348	0.354
6	Minerals, manure, solid, and liquid, leached.....	0.335	0.328	0.358
7	Minerals, nitrate of soda, 5 gm...............	0.265	0.252	0.273
8	Minerals, nitrate of soda, 10 gm..............	0.268	0.264	0.268
9	Minerals, manure, solid fresh; nitrate 5 gm......	0.333	0.332	0.347
10	Minerals, manure, solid, fresh; nitrate, 10 gm....	0.316	0.330	0.350
11	Minerals, manure, solid, and liquid, fresh; nitrate, 5 gm................................	0.301	0.290	0.315
12	Minerals, manure, solid and liquid, fresh; nitrate, 10 gm................................	0.327	0.303	0.312
13	Minerals, manure, solid, leached; nitrate, 5 gm..	0.346	0.350	0.361
14	Minerals, manure, solid, leached; nitrate, 10 gm.	0.335	0.330	0.358
15	Minerals, manure, solid, and liquid, leached; nitrate, 5 gm................................	0.328	0.343	0.364
16	Minerals, manure, solid and liquid, leached; nitrate, 10 gm.........................	0.312	0.330	0.350
17	Minerals, sulfate of ammonia, equivalent to 10 gm. nitrate...............................	0.286	0.286	0.294
18	Minerals, dried blood, equivalent to 10 gm. nitrate.................................	0.276	0.285	0.290
19	Minerals, manure, solid, leached; sulfate of ammonia as in 17...........................	0.351	0.330	0.367
20	Minerals, manure, solid, leached; dried blood as in 18................................	0.338	0.335	0.367
	Average..	0.309	0.303	0.326

The cylinders of series 2 where acid phosphate and potash have been applied without nitrogen, have, with slight exception, made the least increase of any. Next in order of increase are series 7, 8, 17 and 18. Reference to the plan will show that these cylinders receive liberal applications of commercial fertilizers, but no manure. The average gains have been slightly greater on the C cylinders than on the A or B cylinders. This is probably due to the fact that on

the C cylinders two green manure crops have been grown during each five-year period.

These gains over a period of years are significant, when considered in connection with the nitrogen losses which have taken place over the same period. They are also of interest since they bear out, in a striking manner, the general belief that phosphates are not readily lost in the drainage waters.

In this connection it is of interest to note that Dyer's (4) analyses of Rothamsted soils show that the greater part of the excess of phosphoric acid supplied, over that removed in the crops, was still to be found in the top 9 inches of the soil. Dyer summarizes his work in these words: "by far the greater portion of the unconsumed phosphoric acid in the manure is accumulated in the surface soil although for the most part originally soluble in water. In the case of dung there is a considerable descent into the second and third depths of 9 inches, and there is also evidence of a considerable descent into the second and even into the third depths in those cases in which superphosphate has been accompanied by constant dressings of potassium, sodium and magnesium salts. The greater part of the calculated accumulation, however, is found by analysis in the surface soil, and a large proportion of it is found in a condition in which it dissolves in a weak solution of citric acid."

It should be observed that Dyer refers to the Rothamsted soil as a loam which contains much clay.

According to Dyer's figures (4, p. 100) the unmanured Rothamsted plot contained 0.114 per cent phosphoric acid in 1893, and the plot which had received barnyard manure for fifty years contained 0.215 per cent. Therefore, the plowed acre (2,000,000 pounds), manured, contained in 1893, approximately 2000 pounds per acre more phosphoric acid than the unmanured land. The Rothamsted records show that the manure was used at the rate of 14 tons per acre annually for the fifty years. This manure must have supplied at least 5 pounds of phosphoric acid per ton or 3500 pounds for the entire period. Assuming that the crops removed on an average 30 pounds of phosphoric acid per acre annually, 1500 pounds would be accounted for in this way. This subtracted from the 3500 pounds would leave the manured soil with just 2000 pounds more phosphoric acid per acre than the unmanured, which corresponds very closely with the analyses reported above. According to this calculation there must have been practically no loss of phosphoric acid during the fifty years. It is entirely possible, however, that the manure may have contained somewhat more than 5 pounds phosphoric acid per ton, or that the crop may have removed less than 30 pounds per acre, for undoubtedly some phosphoric acid must have been transferred to the second and third 9-inch sections.

After twenty-five years of cropping, our unmanured cylinder soils show an average of about 0.18 per cent phosphoric acid; those which have received acid phosphate but no manure, an average of about 0.27 per cent; and those which have received both acid phosphate and manure, an average of 0.33 per cent. According to the analyses of the original soil the plowed acre (6⅔ inches depth) must have contained about 4500 pounds of phosphoric acid. The annual application of acid phosphate at the rate of 640 pounds per acre would mean approximately 100 pounds of phosphoric acid per acre annually or 2500 pounds for the twenty-five years. This added to the amount present in the beginning gives a total of 7000 pounds.

In the soils of those cylinders which have received the acid phosphate but not manure there is now present, according to analysis, approximately 5400

pounds of phosphoric acid per acre 6⅔ inches. This subtracted from the 7000 pounds leaves 1600 pounds to be accounted for. The crops which have been removed over the period will account for a considerable part of this. The amount thus removed may be calculated with a fair degree of accuracy. Without going into the details of taking the individual cylinder yields for each year the average yields for the different crops for the twenty-five year period may be multiplied by the average percentage of phosphoric acid in the dry matter to obtain the total amount of phosphoric acid thus removed.

Since a part of the cylinders received their phosphoric acid in the form of acid phosphate only (single portion) and a part received it in the form of acid phosphate and manure (double portion) it is necessary to report the average yields for both treatments. The average annual yields were as follows:

CROP	DRY MATTER PER CYLINDER	
	With mineral fertilizers only	With mineral fertilizers and manure
	gm.	*gm.*
Corn (forage), 5 years	300.0	450.0
Oats (grain and straw) ⎱ 10 years	173.6	207.3
Residual corn (forage) ⎰	79.9	133.2
Wheat, 5 years ⎰ Grain	82.1	101.7
⎱ Straw	140.5	190.7
Timothy hay, 5 years	150.0	220.4

Phosphoric acid and potash have not been determined in the crops for each year, but sufficient determinations have been made for the different crops to give a fair average. The results are as follows:

CROP	PHOSPHORIC ACID	POTASH
	per cent	*per cent*
Corn (forage)	0.464	2.20
⎰ Oats (grain and straw)	0.940	1.71
⎱ Residual corn (forage)	0.873	3.42
Wheat ⎰ Grain	1.121	0.50
⎱ Straw	0.227	0.67
Timothy hay	0.441	0.88

From the dry weights and the percentages of phosphoric acid the pounds of phosphoric acid removed per acre by the crops for the twenty-five-year period have been calculated, with the results shown in table 2.

Thus it is seen that of the 1600 pounds previously reported as unaccounted for in the cylinders receiving the mineral fertilizers, only about 1272 pounds have been removed by the crops leaving 328 pounds or an average of 13 pounds per year as held in the subsoil and lost in the drainage waters. The average removed by the crops amounts to about 51 pounds per acre annually.

For those cylinders which have received both manure and acid phosphate, phosphoric acid has been applied at the rate of about 200 pounds per acre annually or 5000 pounds for the 25 years. This added to the 4500 pounds present in the beginning, gives a total of 9500 pounds. By analysis it is found that these cylinders now contain phosphoric acid equivalent to 6600 pounds per acre. This leaves 2900 pounds to be accounted for in crops removed, or otherwise. From table 2 it is found that the crops grown on these cylinders during the twenty-five years, removed 1736.5 pounds of phosphoric acid. Subtracting this from 2900 pounds leaves 1163 pounds fixed in the subsoil and lost in drainage waters. This is an average of about 46 pounds per acre annually which is more than three times the amount thus lost from those cylinders that received the single portion of phosphoric acid.

TABLE 2

Phosphoric acid removed by the several crops for a period of twenty-five years

CROP	P_2O_5 REMOVED PER ACRE	
	With mineral fertilizers only	With mineral fertilizers and manure
	pounds	*pounds*
Corn, 5 years..	222.6	333.9
Oats ⎫ 10 years ⎧................................	522.2	623.6
Residual corn ⎭ ⎩................................	223.1	372.0
Wheat, 5 years ⎰ Grain................................	147.1	182.3
⎱ Straw................................	51.0	69.2
Timothy hay, 5 years................................	105.8	155.5
Total for 25 years......................................	1,271.8	1,736.5

It would be expected that with the heavier applications the loss into the subsoil and drainage waters would be greater.

Dyer (4, p. 111–112) made a similar observation for he says: "The superabundance of phosphoric acid estimated to have been supplied in the dung for fifty years is less satisfactorily accounted for than is the case with the phosphoric acid in the chemically manured plots." He supposes this may be partly accounted for by an over-estimation, for a part of the time, of the proportion of phosphoric acid in the dung, and concludes: "But there appears reason for supposing that there has been a greater descent into the subsoil in the case of the plot dunged for fifty years, than in the case of the chemically manured plots."

A comparison of this work with the nitrogen studies above referred to, shows that it is much easier to maintain and increase the phosphoric acid content of the soil than it is to maintain and increase the nitrogen content. The work brings to our attention the fact that where commercial fertilizers are used at the rate of a ton or more per acre, as is common in many trucking and potato sections, there is a piling up of phosphoric acid in the soil beyond crop requirement.

The question is at once raised as to whether this is necessary or not, and also as to whether there is any danger of increasing the phosphoric acid content of the soil to the point of injury. It is well known that soils may, under some conditions, contain soluble compounds of aluminum to such an extent as to render them toxic. In such cases heavy applications of soluble phosphates would precipitate the aluminum and render harmless the toxic substances. However, the same results could be accomplished, and at less expense, by the use of lime in some form, and the lime would at the same time serve the further purpose of making the soil better fit for the growing of clover and other legumes.

As to the second point—the possible injury to crops from too great an accumulation of phosphoric acid in the soil—there is need of further investigation.

Sherwin (15) has called attention to the depressing effect that acid phosphate without potash, had on corn grown on drained swamp land at Terra Ceia, North Carolina. He observed a greater discoloration of the nodal tissues of the stalk and a greater accumulation of iron where the phosphorus was used without kainit than where kainit or kainit and nitrate of soda were used with the phosphorus, and points out that the increase in yield was roughly in proportion to the depression of iron accumulation. Sherwin refers to a statement by Hoffer to the effect that the root rot (referring to the root rot of corn) is related to metal poisoning, and the greater the accumulation of iron within the tissues the greater the damage from root rot. He believes that potash enables the plant to withstand otherwise toxic amounts or compounds of iron: "Any treatment therefore," he says, "which keeps the iron out may be expected to decrease root rot and increase the yield of corn. The observed facts are that the discoloration due to iron is less and the yield greater when kainit and nitrate of soda are used, and that the discoloration is greater and the yield less when acid phosphate is used." Among other conclusions he finds that: "Acid phosphate retards the entrance of potash into the plant, hence aids in the accumulation of toxic iron."

This, however, is not in full agreement with conclusions reached by Hoffer and Carr (7) who state that "in all cases studied so far the application of available phosphates produced plants which were better and more resistant to the root rots."

In this connection Burgess and Pember (1, p. 38) say: "It thus appears that acid phosphate renders soluble aluminum salts non-toxic largely by counteracting their evil effects within the plants themselves after they have been absorbed. Thus a very important function of soluble phosphates when applied to acid soils may be in nullifying the effects of such toxic substances as dissolved aluminum, manganese and ferrous iron."

In a potato fertilizer experiment carried out on a loam soil at this station, in coöperation with the Bureau of Plant Industry, United States Department of Agriculture, the five year average yield of potatoes from eight plots that received nitrogen, or nitrogen and potash without phosphoric acid, or with phosphoric acid at the rate of only 45 pounds per acre, was 124.6 bushels per acre as against 117.5 bushels for the five-year average of six plots which received nitrogen or nitrogen and potash, and phosphoric acid at the rate of 90, 135, and 180 pounds per acre. It would thus appear that the heavier applications of phosphoric acid depressed rather than increased the yield of potatoes. In this connection it may be explained that in the better potato sections it is customary to use phosphoric acid at the rate of 128 to 160 pounds per acre every year.

The advisability of such heavy applications annually may well be questioned when it is considered that potatoes require less of phosphoric acid than either nitrogen or potash, and that phosphoric acid is lost in the drainage waters in less amounts than either of the other elements. Under these conditions an accumulation of phosphoric acid in the soil is inevitable and this may finally reach a point where it becomes detrimental rather than beneficial.

TOTAL POTASH (K₂O) IN SOILS AND CROPS

Total potash was determined in samples of soil from twenty-one of the sixty cylinders, that is, in each of the three cylinders of seven different series. The results are reported in table 3.

The determinations show a uniformity that indicates that the different treatments have not influenced the total potash content of the soil to a marked degree. This is well illustrated by comparing the figures for series 1 and 2. Series 1 has received no potash-containing fertilizer during the entire period, while series 2 has received muriate of potash at the rate of 320 pounds per acre every year or a total of 4000 pounds of actual potash (K_2O) for the twenty-five years. The analyses, however, show the soils of the two series to contain practically equal amounts of potash.

Series 12 receives manure at the rate of 16 tons per acre annually in addition to the 320 pounds of muriate of potash, and since 1 ton of manure will supply

TABLE 3

Potash (K_2O) in cylinder soils (sampled 1920)

SERIES	CYLINDER A	CYLINDER B	CYLINDER C
	per cent	*per cent*	*per cent*
1	2.11	2.11	1.94
2	1.93	2.12	1.96
6	2.45	2.51	2.13
8	2.20	1.76	2.21
12	2.02	2.13	2.20
17	2.15	2.29	2.36
20	2.07	1.99	2.13
Average......	2.13	2.13	2.13

about 10 pounds of potash the 16 tons would add an amount equal to the amount furnished by the 320 pounds of muriate of potash. Thus, for example, the cylinders of series 12 which receive both manure and muriate of potash, receive approximately twice as much potash as those of series 8 which receive the muriate of potash only. But the average percentage of potash in the soils of series 8 is practically the same as the average for series 12.

The reason for the failure of the potash treatments to show important differences in the potash content of the soil, even after a period of twenty-five years, must be found largely in the very great difference between the total amount of potash in the soil and the total amount applied. In other words, the total potash in the soil is so great, compared with the amount applied, that the latter has little influence on the percentage found in the soil. To further illustrate this point it may be pointed out that the original soil contained 2.63 per cent of total potash, equivalent to 52,600 pounds for the plowed acre. The amount applied during the twenty-five years—4000 pounds—even if added all at one

time would change the analysis by only a fraction of a per cent, a change which would perhaps come within the limit of error.

But during the twenty-five years there have been losses which must be taken into consideration. The losses through the removal of crops can be calculated with some degree of accuracy, but the losses into the lower depths of the soil and through drainage waters can only be approximated.

From the average weights of the crops removed and the average percentage of potash in the crops, previously reported, we may calculate the total amount of potash removed in this way. These figures are shown in table 4.

We are at once struck with the large amount of potash removed in comparison with the amount of phosphoric acid. In each case (single and double applications of potash) the amount of potash removed by the crops is nearly three times the amount of phosphoric thus removed. The average amount of potash removed annually by crops where mineral fertilizers only were used is

TABLE 4

Potash removed by the several crops for a period of twenty-five years

CROP	K_2O REMOVED PER ACRE	
	With mineral fertilizers only	With mineral fertilizers and manure
	pounds	*pounds*
Corn, 5 years..	1,056.0	1,584.0
Oats ⎫ 10 years ⎧	949.9	1,134.4
Residual corn ⎭ ⎩	875.5	1,457.2
Wheat, 5 years ⎧ Grain...............................	65.7	81.4
⎩ Straw...............................	150.6	204.4
Timothy hay, 5 years.................................	211.2	310.3
Total for 25 years...................................	3,308.9	4,771.7

132.4 pounds per acre. This means nearly three-fourths of the amount applied, or to state it another way, 4000 pounds of potash (K_2O) were applied during the twenty-five years, and 3309 pounds were taken out through the crops removed. This leaves 691 pounds of the amount *applied* or an annual average of 27.6 pounds per acre which must be accounted for in the subsoil or lost in drainage waters.

For the same period the crops taken from the cylinders that received the double application of potash (8000 pounds of K_2O for twenty-five years) removed 4772 pounds of potash or an average of 191 pounds per acre per annum. Thus there is an unaccounted-for loss of *applied* potash amounting to 3228 pounds or an average of 129 pounds per acre per year, as against 27.6 pounds per acre where the single portion was used. That there were also heavy losses of the original soil potash is evident from the fact that the soils now contain less potash than when the experiment was started, although the crops have removed less than has been applied.

The losses may be approximated as in the case of phosphoric acid. The figures may be summarized as follows:

	CYLINDERS RECEIVING SINGLE APPLICATION OF POTASH	CYLINDERS RECEIVING DOUBLE APPLICATION OF POTASH
	pounds per acre	*pounds per acre*
Potash (K_2O) originally present in soil......................	52,600	52,600
Potash applied.....................................	4,000	8,000
(a) Total..	56,600	60,600
(b) Potash now present in soil (average)..................	42,600	42,600
Total potash lost and removed in crops (a − b)...........	14,000	18,000
Total potash removed in crops (cf. table 4)...............	3,309	4,772
Potash apparently lost in subsoil or in drainage waters........	10,691	13,228
Average annual amount of potash removed by crops.........	132.4	190.9
Average annual loss (*apparent*) of potash in subsoil or through drainage waters..	427.6	529.1

The averages representing the removal of potash by crops are larger than most authorities give for the crops in question. In explanation of this it must be remembered that on account of the special care given to the work the yields have been larger than are generally realized in general farm work. Also the potash applications have been heavier than those used in general farm practice, and under such conditions there is a tendency for most crops to utilize more potash than is really required, that is, there is more or less "luxury" consumption.

The *apparent* losses into the subsoil and through drainage waters are likewise large. This must be attributed in part to the heavy fertilization and in part to the fact that the subsoil is a coarse gravelly material which gives good drainage and therefore permits rather rapid loss of soluble substances.

It is thus evident that potash is not as firmly held in the top portions of the soil as is phosphoric acid, and it follows that excessive applications cannot be made with the hope that the greater portion of the amount beyond the crop's requirement, will be held in the cultivated portion of the land. Much of it, however, may be held in the lower portions of the soil.

Attention may be called to the very high percentage of potash in the residual corn. As previously explained this crop follows the oats and is planted very thick and harvested as forage before it matures. It would thus appear that corn taken at this stage is much richer in potash than stalks harvested at maturity. Taking two crops in one season—oats and residual corn—makes an unusually heavy draught upon the potash of the soil, amounting to a yearly average for the ten combined crops, of 182.5 pounds per acre for the cylinders that receive the single application of potash, and 259.6 pounds per acre for those that receive the double application.

The main corn crop which received the double portion of potash has drawn more heavily on the potash of the soil than the oats and residual corn. The average yield of 450 gm. of dry matter per cylinder is equivalent to 14,400 pounds per acre and with a potash content of 2.2 per cent, the crop would remove potash at the rate of 317 pounds per acre. This is far in excess of the usual potash application for corn or even for corn silage, but in a soil well supplied with potash, as this is, it should be practicable to draw somewhat upon the reserve supplies without permanent injury, inasmuch as the subsoil often contains more potash than the surface soil.

In discussing the removal of plant food by crops at the Rothamsted Experimental Station, Hall (6) states that the average crop on the unmanured plot removes annually about 14 pounds of potash per acre. The crops from plot 2 which receives farmyard manure at the rate of 14 tons per acre, remove 52 pounds of potash per acre. It is pointed out that analyses of the soil show that enormous reserves ot plant food have been accumulated in the soil of this plot, the nitrogen and phosphoric acid both being about double that in the unmanured plot and the potash showing a very considerable increase. It should be remembered, however, that Indian corn, which is a heavy potash feeder, was not one of the crops included in the Rothamsted experiment.

Hall (6) further says: "Again, as regards the potash, the average removal from the unmanured plot under rotation is 13.2 pounds whereas the continuous wheat plot similarily unmanured loses 14.3 pounds and the continuous barley plot 11.6 pounds per acre per annum." With reference to the removal of potash through crops in rotation, Hall finds that a rotation of swedes, barley, fallow or beans or clover, and wheat removes about 200 pounds or an average of nearly 50 pounds per acre per annum. He assumes that 15 tons of manure which were applied for this rotation supplied 150 pounds of potash but even though the manure does not fully replace the potash removed by the crops of the rotation he thinks it would not be necessary to supply potash salts on a soil as high in potash as that of Rothamsted is.

"The reserves of potash," he says, "in such a strong soil are enormous—at least 50,000 pounds per acre in the top 9 inches of soil, of which 12,000 pounds is soluble in hydrochloric acid—and a little of it becomes available every year under the action of the weathering induced by cultivation."

Dyer (4, p. 124) in discussing "Results of Investigations on the Rothamsted soils" sums up his discussion on potash as follows:

"It has usually been considered that potash is pretty firmly retained in the surface soil on land containing a fair proportion of clay. That this is the case, as compared with sodium salts, has often been shown, and, apart from earlier investigation, was clearly brought out in the drainage water analyses of the late Dr Voelcker, just referred to; but, as we have seen, even these analyses showed a considerable loss of potash in drainage in certain cases, and it is evident from the results of the analyses of the soils and subsoils that though, relatively to sodium salts, potassium salts readily become fixed in clay soils—often, probably, passing into a very stable insoluble form—they are nevertheless far more "migratory" than phosphoric acid."

Lyon and Bizzell (11, p. 55) have studied the removal of potash in drainage waters and crops from large tanks and have reported the loss through drainage and the removal of crops, from eight such tanks, the drainage results covering a period of five years and the crop results the first four of the five years. Averages for the eight tanks are as follows:[a]

Potash in drainage.....................52.9 pounds (43.9 pounds K) per acre
Potash in crops.......................95.4 pounds (79.2 pounds K) per acre
    Total potash.......................148.3 pounds (123.1 pounds K) per acre

[a] Tanks 4 and 8 omitted from average on account of incomplete results.

In discussing the effect of plant growth on the removal of potash they say: "Evidently native potassium is not sufficiently soluble in the soil water to supply the needs of the crops produced, as an average of only 61 pounds of potassium was leached annually from an acre of unplanted soil to offset the 79.2 pounds removed by the average crop from the same area, while there was an average of 367.4 pounds of calcium leached through each acre of unplanted soil and only 12.6 pounds removed in the average crop."

In a later bulletin, Lyon and Bizzell (12) report the average annual removal of potash from two planted tanks to be as follows:

Potash in drainage water................88.2 pounds (73.2 pounds K) per acre
Potash in crops........................41.1 pounds (34.1 pounds K) per acre
  Total potash........................129.3 pounds (107.3 pounds K) per acre

Thus it will be observed that the *total* losses (drainage and crops) shown in their work, are not quite so great as the losses which we have charged against the *applied* potash. In addition to this loss of applied potash our experiments have shown a serious depletion of the stock of original soil potash.

TOTAL LIME (CaO) IN THE SOILS

Reference to the earlier reports on this work (10) will show that the soil of all the cylinders received the same lime treatment in the beginning. This treatment was not varied during the first ten years of the experiment. With the beginning of the third five-year period, lime was omitted from the A cylinders, but the B and C cylinders were limed at the rate of two tons of carbonate per acre. This treatment has been continued at intervals of five years to the present time.

By analysis the original soil contained 0.807 per cent of total lime (CaO). The samples collected in 1920 after twenty-three years of cropping and fertilizer treatment have now been analyzed with the results shown in table 5.

The effect of the lime treatment on the lime content of the soil of the B and C cylinders for all series is very apparent, the average percentage in both cases being somewhat above the percentage in the original soil. On the other hand the average percentage of lime in the A cylinders is distinctly less than the percentage in the original soil. The lowest percentage (0.425) was found in 17 A where ammonium sulfate has been used continuously without lime, and the highest percentage (0.959) in cylinders 6, 13 and 14 C, where manure and minerals in the one case and manure, minerals and nitrate of soda in the other two have been used continuously.

The difference between the lowest and the highest percentage is equivalent to about 5 tons of lime per acre. In terms of crops produced, it is a difference between heavy yields and no crops, the soil of 17 A having become so toxic as to practically inhibit growth.

It may here be pointed out that the soil represented by this cylinder appears to have lost lime at the rate of approximately 7600 pounds, on the basis of the plowed acre, during the twenty-three-year period,[3] or an average annual loss of over 300 pounds per acre in addition to that which was supplied in the acid

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[3] Lime determinations were made on the 1920 samples.

phosphate used at the rate of 640 pounds per acre. If the lime content in this
be put at 100 pounds per acre, the total loss is brought to well over 400 pounds
of lime (CaO) per acre, equivalent to approximately 800 pounds of calcium
carbonate. A part of this loss, of course, must be accounted for by the crops
that have been removed.

TABLE 5

Per cent lime (CaO) in cylinder soils (sampled 1920)

SERIES	SPECIAL TREATMENT	CYLINDER A	CYLINDER B	CYLINDER C
		per cent	*per cent*	*per cent*
1	Check....................................	0.493	0.877	0.932
2	Minerals.................................	0.493	0.767	0.822
3	Minerals, manure, solid, fresh..............	0.713	0.987	0.932
4	Minerals, manure, solid and liquid, fresh......	0.575	0.850	0.877
5	Minerals, manure, solid, leached............ .	0.740	0.904	0.932
6	Minerals, manure, solid and liquid, leached....	0.575	0.904	0.959
7	Minerals, nitrate of soda, 5 gm..............	0.575	0.850	0.850
8	Minerals, nitrate of soda, 10 gm...........	0.575	0.808	0.794
9	Minerals, manure, solid, fresh; nitrate, 5 gm....	0.658	0.932	0.932
10	Minerals, manure, solid, fresh; nitrate, 10 gm....	0.658	0.850	0.850
11	Minerals, manure, solid and liquid fresh; nitrate 5 gm......................................	0.589	0.863	0.904
12	Minerals, manure, solid and liquid, fresh; nitrate, 10 gm.............................	0.617	0.794	0.822
13	Minerals, manure, solid, leached; nitrate, 5 gm..	0.617	0.937	0.959
14	Minerals, manure, solid, leached; nitrate, 10 gm.	0.726	0.877	0.959
15	Minerals, manure, solid and liquid, leached; nitrate, 5 gm.............................	0.589	0.904	0.877
16	Minerals, manure, solid and liquid, leached; nitrate, 10 gm......................... .. .	0.630	0.850	0.932
17	Minerals, sulfate of ammonia, equivalent to 10 gm. nitrate...........	0.425	0.672	0.767
18	Minerals, dried blood, equivalent to 10 gm. nitrate.................................	0.562	0.822	0.932
19	Minerals, manure, solid, leached; sulfate of ammonia as in 17.................	0.562	0.863	0.918
20	Minerals, manure, solid, leached; dried blood as in 18................................	0.548	0.822	0.891
Average	....	0.596	0.856	0.892

It is of interest to compare the figures for series 17 with those for series 19.
The latter it will be noted received the same amount of sulfate of ammonia as
the former, but the loss of lime has been much less than the loss from series 17.
It would appear therefore that the manure in some way tends to overcome the
toxic influence of sulfate of ammonia when lime is lacking, and also tends to
check the loss of lime.

This, in a general way, confirms our results from field experiments where ammonium sulfate has been used continuously without lime, and also the results reported from Rothamsted and elsewhere.

In this connection Hall (6, p. 238–239) has this to say: "Where ammonium salts like the sulfate and chloride are applied as a manure the soil suffers a great loss of calcium carbonate, the calcium being removed in the-drainage water combined with the sulfuric or hydrochloric acid of the manure. This reaction is the necessary precedent to the arrest of the ammonia in the soil and its subsequent nitrification. In the absence of a sufficiency of calcium carbonate in the soil to bring about this reaction, ammonium salts become injurious to plant life. . . .

"Since the healthy condition of the soil depends on a due proportion of calcium carbonate being present, those losses caused by the use of natural and artificial manures are of the greatest importance; many of our fertile soils may easily lose much of their power of producing unless their proportion of calcium carbonate is restored by judicial liming at intervals.

"Determinations of the calcium carbonate in samples of soil taken at various intervals between 1865 and 1904 indicate that on the manured plots the normal loss of calcium carbonate in the drainage water amounts to about 1000 pounds per acre. When ammonium salts are used as a manure the loss is increased by the amount required to combine with the combined acid in the manure."

On the same point Warington (17, p. 100) says: "The loss of calcium carbonate which a soil suffers when continuously manured with ammonium salts is a point which should always be borne in mind. It has been found necessary at Rothamsted to apply a heavy dressing of chalk or lime to those plots in the grass experiment which has long received ammonium salts."

Russell (14) in discussing the amount of calcium carbonate lost from the soil says: "Calcium carbonate is not a permanent constituent of the soil, but changes into the soluble bicarbonate and washes out into the drainage water; the average loss per acre per annum throughout England and Wales has been estimated at 500 pounds, and at Rothamsted on the arable land at 800 to 1000 pounds. The rate of loss is influenced by the treatment, being increased by the use of ammonium sulfate and decreased by dung and by a growing crop; it is much less on pasture than on arable land."

Cylinders 1 A and 2 A show the same amount of loss, the percentage in 1920 being 0.493 as against 0.807 in 1898. But 1 A has received no lime, fertilizer, or manure since the first application of lime to all cylinders when the work was started, whereas 2 A has received acid phosphate at the rate of 640 pounds per acre every year, or nearly 15,000 pounds up to and including the 1920 application, and muriate of potash at the rate of 320 pounds per acre, or a little over 7000 pounds for the twenty-three years.

Thus through the acid phosphate used, a considereble quantity of lime has been added to the soil but not nearly enough to offset the losses. In this connection it is significant that there is less lime in the soil of 2 B and 2 C than in that of 1 B and 1 C, notwithstanding the fact that the former have received acid phosphate while the latter have received no fertilizer. The explanation probably lies in the fact that the cylinders of series 2 have received muriate of potash along with the acid phosphate. The potash of the muriate would have a tendency to replace the lime which would go out in the drainage waters as calcium chloride. A part of the loss from series 2 can be accounted for in the

larger crops produced by these cylinders. It would thus appear that the absence of a heavy crop and the consequent loss through leaching constitutes a greater drain upon the supply of lime in the soil than the removal of lime in the crops. This is in accord with Russel's statement (14, p. 181) when he says: "The exhaustion of the soil is, therefore, not due to the removal of the crop but to cultivation."

With few exceptions, the B and C cylinders which have received both acid phosphate and manure contain a higher percentage of lime than those that have received only the acid phosphate. This is illustrated by comparing the figures for series 9 and 10 with those for 7 and 8 and series 2 with those for series 3.

Where the loss of lime has occurred it has come about through its removal in crops or in drainage waters, since the cylinders do not permit of surface washing.

TOTAL MAGNESIA (MgO) AND MANGANESE (Mn_3O_4) IN THE SOILS

Magnesia and manganese have been determined in the three soils of series 2, 6, 8, 12, 17 and 20, these being considered fairly representative of the entire lot. The results are shown in table 6.

TABLE 6

Magnesium and manganese in cylinder soils

SERIES	CYLINDER A		CYLINDER B		CYLINDER C	
	MgO	Mn_3O_4	MgO	Mn_3O_4	MgO	Mn_3O_4
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
2	1.46	0.265	1.57	0.219	1.52	0.274
6	1.51	0.256	1.59	0.256	1.66	0.247
8	1.60	0.256	1.55	0.312	1.36	0.274
12	1.51	0.237	1.47	0.265	1.59	0.126
17	1.47	0.312	1.54	0.312	1.63	0.256
20	1.42	0.330	1.43	0.107	1.62	0.274
Average....	1.50	0.276	1.53	0.245	1.56	0.242

Magnesia (MgO)

The original soil contained 2.24 per cent magnesia whereas the present average is about 1.5 per cent. During the twenty-five year period no magnesium compounds have been applied to the soil except such as may have been contained in the manure used and a small amount occurring as an impurity, in the calcium limestone applied to B and C cylinders. Judging from the analyses neither the manure nor the lime contributed very much magnesia, since the magnesium content of the soil is about the same where lime and manure were used as where they were omitted.

The loss of magnesia in terms of per cent does not seem great but calculated on the basis of the plowed acre it amounts to approximately seven tons for the

entire period, or an annual average of between 500 to 600 pounds per acre. This would appear to be a much greater loss than was found by Lyon and Bizzell (12, p. 50) who computed the loss of magnesia through drainage water, and in crops taken from tanks with perfect drainage conditions. In most cases they found the loss to be less than 100 pounds of magnesia per acre annually. It must be pointed out, however, that their soil contained only about one-third of one per cent of magnesia whereas the soil under observation contained originally more than two per cent. Furthermore, the cropping system employed on this soil has been very heavy, two crops being grown during two of the five years of each rotation period.

McIntire and his associates (13) working with a loam soil in tanks having perfect drainage conditions found losses of magnesia equivalent to 100 to 200 pounds calcium carbonate per acre annually where no magnesium compounds were applied; where magnesia was applied in amounts equivalent to 3750 pounds calcium carbonate per acre, the loss in one case was equivalent to more than 1000 pounds of calcium carbonate per acre.

Collison (3) also worked with soil in tanks with perfect drainage conditions and found losses of magnesia in drainage waters amounting to approximately 200 pounds per acre in eight months time. In this case the soil was Norfolk sand and naturally very deficient in basic materials.

From these experiments it must be evident that with long continued cultivation and cropping, soils that naturally contain a small percentage of magnesia, will finally become very thoroughly depleted of their stock of this element. It is indeed conceivable that, in some cases, the supply may become so low as to actually limit crop production.

It may be pointed out that the soil used in this experiment now has a lime magnesia ratio of approximately 1:2.

Manganese (Mn_3O_4)

The percentage of manganese in the soil is low and varies within rather narrow limits amounting to about 0.25 per cent to 0.3 per cent. It probably exists largely in the silicate form and it is doubtful if it has any particular significance in connection with crop yields.

SOIL REACTION

Definite changes have been brought about in the soil reaction by the lime and fertilizer treatments. Determinations of the lime requirement by the Veitch method, and hydrogen-ion determinations by the colorimetric method have been made on the samples taken in 1920. The results of these determinations are reported in table 7.

By both tests the soils of all the A cylinders are acid. For the majority the requirement varies from 1400 to 2000 pounds of lime (CaO) per acre. It may be pointed out that cylinders 17 A and 19 A, where ammonium sulfate has been

used continuously, are the most acid. Both of these show a lime requirement of 2800 pounds per acre. But they differ decidedly in the matter of crop yields. The soil of 17 A is in such bad condition that practically no crops are produced, while 19 A which receives manure in addition to the ammonium sulfate produces each year a fair crop. It is quite evident, therefore, that the manure applied to 19 A counteracts to some degree the toxic condition resulting from the continued use of ammonium sulfate without lime or manure.

In view of the fact that acid phosphate has sometimes been given credit for increasing the acidity of the soil, it is of interest to call attention to the fact

TABLE 7

Lime requirement (CaO by Veitch method) and pH values on cylinders soils collected in the fall of 1920

SERIES	A—UNLIMED		B—LIMED		C—LIMED	
	Lime requirement	pH value	Lime requirement	pH value	Lime requirement	pH value
1	1,400	6.2	0	7.3	0	6.9
2	1,600	6.2	0	7.0	0	6.9
3	1,600	5.7	0	6.8	0	6.8
4	2,000	5.5	0	6.8 ·	0	6.7
5	1,800	5.7	0	6.8	0	6.8
6	1,800	5.7	0	6.9	0	6.8
7	1,600	6.0	0	7.0	0	6.9
8	1,400	6.1	0	7.0	0	6.8
9	1,400	5.8	0	6.9	0	6.8
10	1,600	5.8	0	6.9	0	6.7
11	2,000	5.3	0	6.9	0	6.8
12	2,000	5.5	0	6.8	0	6.8
13	1,800	5.8	0	6.8	0	6.8
14	1,800	6.0	0	6.8	0	6.9
15	1,600	5.8	0	6.7	0	6.8
16	1,600	6.0	0	6.8	0	6.9
17	2,800	4.9	0	6.7	200	6.5
18	1,800	5.4	0	6.8	0	6.7
19	2,800	5.1	500	6.6	500	6.7
20	2,000	5.4	0	6.7	0	6.7

that the soil of cylinder 1 A, which has received no fertilizer of any kind during the entire period, has the same pH value and essentially the same lime requirement as that of 2 A which has received acid phosphate at the rate of 640 pounds per acre annually or nearly 15,000 pounds during the twenty-three years.

Surely if acid phosphate increases acidity its effect should have been shown in the soil of cylinder 2 A in this time.

With one exception, cylinder 19 B, the B cylinders show no lime requirement, and nearly all of them are very close to the neutral point as shown by the colori-

metric method for hydrogen-ion concentration, the pH values nearly all ranging between 6.8 and 7.0. With two exceptions, 17 C and 19 C, the C cylinders show no lime requirement and nearly all show pH values ranging from 6.7 to 6.9.

From these results it is quite evident that two tons of ground limestone applied once every five years has been quite sufficient to keep the soil near the neutral point. There is no indication that this amount is excessive.

SUMMARY

Cylinder soils which have been heavily fertilizer and cropped under controlled conditions for a period of twenty-five years, have on analysis, shown a gain in total phosphoric acid content.

During this period more phosphoric acid was applied to the soil than was removed by the crops.

The soil which has received phosphoric acid at the rate of 100 pounds per acre shows but little actual loss of this constituent; that is, the amount now present as shown by analysis plus the amount removed by the crops of the twenty-five-year period, is almost equal to the amount originally present plus the amount that has been added in the fertilizer for the period. The apparent actual loss thus noted amounts to about 13 pounds of phosphoric acid per acre annually. Undoubtedly a part of this has been retained by the subsoil.

Where phosphoric acid was used at the rate of 200 pounds per acre the apparent loss was more than three times as much as the loss when the single portion (100 pounds per acre) was used.

Larger crops were obtained with the double than with the single portion of phosphoric acid, but the yield was not increased in direct proportion to the increase in fertilizer. Where the single portion of phosphoric acid was used the average amount of phosphoric acid withdrawn annually by the crops amounted to 51 pounds per acre and where the double portion was used the average amount thus removed was about 70 pounds per acre.

The five corn crops (forage) gave an average annual return of phosphoric acid equal to 66.8 pounds per acre.

The work indicates that with average fertilizer treatment very little phosphoric acid is actually lost in the drainage waters; the heavier the application, however, the greater the loss.

It is suggested that in the case of some crops where heavy applications of acid phosphate are made annually the accumulation of phosphoric acid in the soil may finally have a detrimental effect.

Determinations of potash in the soil from a number of the cylinders show a loss of this constituent, although potash has been used each year in amounts considerably above the general average for the crops used in this experiment.

Analysis shows that the soil which originally contained about 2.6 per cent potash now contains, on an average, a little more than 2 per cent of potash.

The total amount of potash applied during the twenty-five years was so small, in comparison with the total amount originally present, that this has apparently had little to do with changing the potash content of the soil. Evidently the greatest change has come about through the removal of potash in the crops and in drainage waters.

From those cylinders that received the single portion of potash the crops have removed potash at the average rate of 132.4 pounds per acre annually, and from those that received the double portion they have removed an annual average of 191 pounds per acre.

The corn crop has been the heaviest user of potash averaging over 200 pounds per acre annually where the single application of potash was made and over 300 pounds per acre where the double application was made. The oats and residual corn follow next in order.

Under heavy fertilization general farm crops remove large amounts of potash. Under such conditions the loss of potash through drainage waters is also large.

The soil from all the cylinders which have not been limed shows a lower percentage of lime (CaO) than the original soil.

With five exceptions all the cylinders that have been limed (B and C cylinders) show a higher percentage of lime than was contained in the original soil. The greatest loss of lime is noted from cylinder 17 A where ammonium sulfate has been used continuously without lime or manure.

Of the five limed cylinders which show some loss, or have remained constant in lime content, cylinder 17 B (ammonium sulfate treatment without manure) shows the greatest loss.

Of the limed cylinders, 2 B and 2 C (acid phosphate and muriate of potash without nitrogen) show a lower lime content than 1 B and 1 C which received no mineral fertilizers.

Magnesia was determined in certain of the soils although this element was not applied as a fertilizer. Small amounts were introduced, however, through the manure and as an impurity in the calcium limestone. The soil originally contained 2.24 per cent of magnesia (MgO) but now contains only about 1.5 per cent of this constituent.

Some very definite changes have been brought about in the soil reaction by the lime and fertilizer treatment.

The soil of all the unlimed cylinders is now acid, the lime requirement varying from 1400 to 2800 pounds per acre and the pH value varying between 4.9 and 6.2.

With slight exceptions the soils of the limed cylinders have no lime requirement and show pH values varying from 6.5 to 7.3.

In the unlimed group, cylinder 17 A shows the highest lime requirement. The soil of this cylinder has become so toxic that no field crop will grow to maturity. There is nothing in this work to indicate that the continued use of acid phosphate causes the soil to become more acid.

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THE AERATION OF SOILS AS INFLUENCED BY AIR-BAROMETRIC PRESSURE CHANGES

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INTRODUCTION

Aeration of soils is considered as one of the essential factors of plant growth. It is well known that for a healthy development and normal functioning, the roots of plants require the presence of free oxygen. It is also well recognized that carbon dioxide which has its main seat of formation in the soil in strong concentrations may be poisonous or may form an unfavorable environment for the best development of the roots of plants. Furthermore, there are various other biological and chemical processes going on in the soil such as the respiration of lower organisms, decay and oxidation of organic and inorganic material, nitrification, etc., which must have access to free oxygen for their proper functioning. In the process of aeration, therefore, oxygen is supplied to the soil which goes to satisfy these various demands.

There are five distinct factors which influence, to a greater or less degree, the process of aeration of soils—diffusion, temperature, rainfall, wind, and atmospheric pressure. Our present knowledge concerning the relative importance of these various factors on soil aeration is based almost entirely on theoretical and *a priori* considerations and very little on experimental facts. The present general opinion seems to be that soil aeration is dependent almost entirely on the factor of diffusion and that the other factors play no or only a slight part in the process.

In conducting various studies on soil temperature, the effect of temperature on soil aeration has been investigated. It was found that temperature changes had a very large influence on soil aeration. This influence is due not only to expansion and contraction of gases but also to the absorption of gases by the soil at different temperatures, and to the aqueous vapor.

From the work on soil temperature and from certain soil observations we have come to feel that atmospheric pressure must play a larger influence on soil aeration than is commonly attributed to it. In order to ascertain definitely, however, whether or not such was the case, and if so to what extent, it was decided to subject the problem to an investigation. The investigation was greatly facilitated by using barographs in the soil, at different depths, to study the influence of barometric pressure upon soil aeration. The results show that

atmospheric pressure changes must have considerable influence on the aeration of soils. It is the purpose of this paper, therefore, to present the experimental data obtained together with the conclusions to which they lead.

MODE OF PROCEDURE

The barographs used in studying the influence of barometric pressure on soil aeration were the same as those used for recording the atmospheric pressure. They were of the latest type and proved to be very accurate and very satisfactory. The method of procedure consisted of digging a hole about 10 feet deep, and about 3 feet square. On one side of the hole at various depths there were excavated small caves in which the barographs were placed. For protection against injury and from rainfall, the barographs were rested on a metal plate and covered above with a metal box. After they were in place, the main hole was filled again. In order that the atmospheric pressure might not reach the barographs through the disturbed soil, every layer of soil of about 3 inches was vigorously compacted by means of a cement tamper. In some instances water was added to help make the layer more impervious to the penetration of air. It is believed that the disturbed material in the heavier type of soil was by this form of compaction made absolutely impervious to the penetration of air and that the atmospheric pressure could not reach the barographs through this compacted column of soil.

Five different types of soil were used in the investigation—sand, sandy loam, loam, clay loam and clay, situated in different localities. In some of these soils barographs were placed at the same time at three different depths: 2 feet, 6 feet and 10 feet. In other cases they were placed at 2 and 10 feet only. For an accurate and dependable comparison between the atmospheric pressure and that in the soil at the various depths, the atmospheric pressure was recorded by a similar barograph placed right on the surface of the soil and right above the buried barographs. All the barographs were standardized and set for the same time. They were allowed to run for a week, and those in the soil had to be unburied.

EXPERIMENTAL

In figures 1 to 5 inclusive are presented photographs of the actual and original charts as recorded by the barographs for the soils and for the air. They reveal at once two outstanding and very interesting facts. First, atmospheric pressure changes take place in the soil as well as in the air. Second, the magnitude of these changes and the time in which they occur are exactly the same in the soil as in the air. The charts show that in all soils, and in all depths—even down to 10 feet—atmospheric pressure changes occurred and that these atmospheric pressure changes are exactly the same in every respect as those in the air. This latter fact is rather remarkable not only *per se* but also because it is just the opposite from what might have been expected. Buckingham, (2) for instance, says:

In reality the barometric changes have a finite speed and the soil offers some resistance to the passage of air through it; hence the pressure at any point in the soil will vary less than the
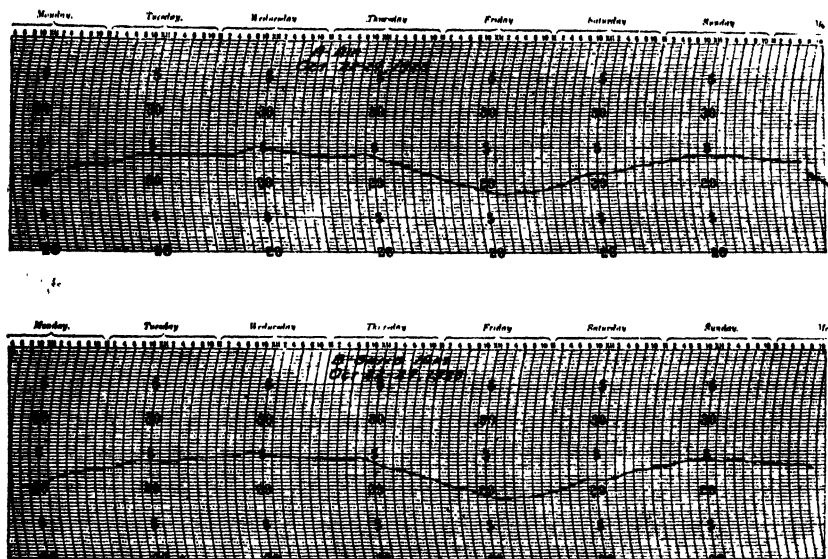
FIG. 1. DAILY MARCH OF BAROMETRIC PRESSURE IN AIR AND IN SAND AT A DEPTH OF 10 FEET
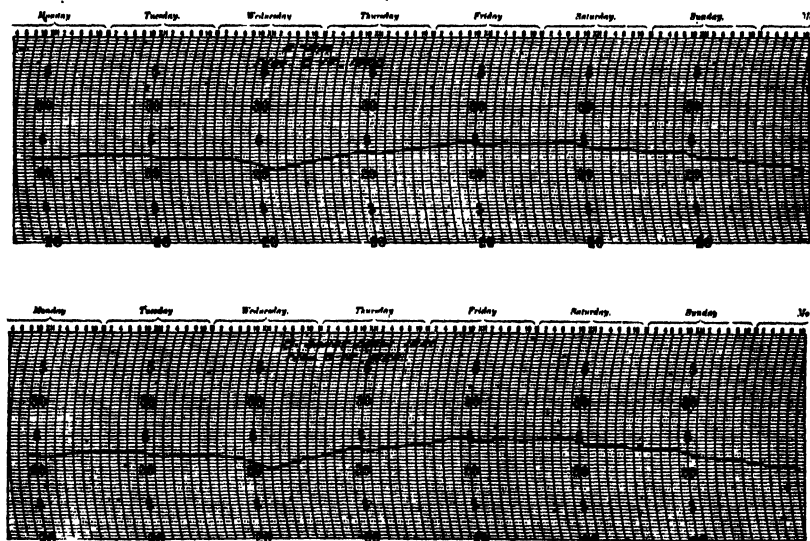
FIG. 2. DAILY MARCH OF BAROMETRIC PRESSURE IN AIR AND IN SANDY LOAM AT A DEPTH OF 10 FEET

outside pressure, and the amplitude of the variation will decrease as we go deeper down into the soil. Furthermore, there will be a certain amount of time lag, by which we mean that the variations of pressure at any point in the soil will not be simultaneously with the
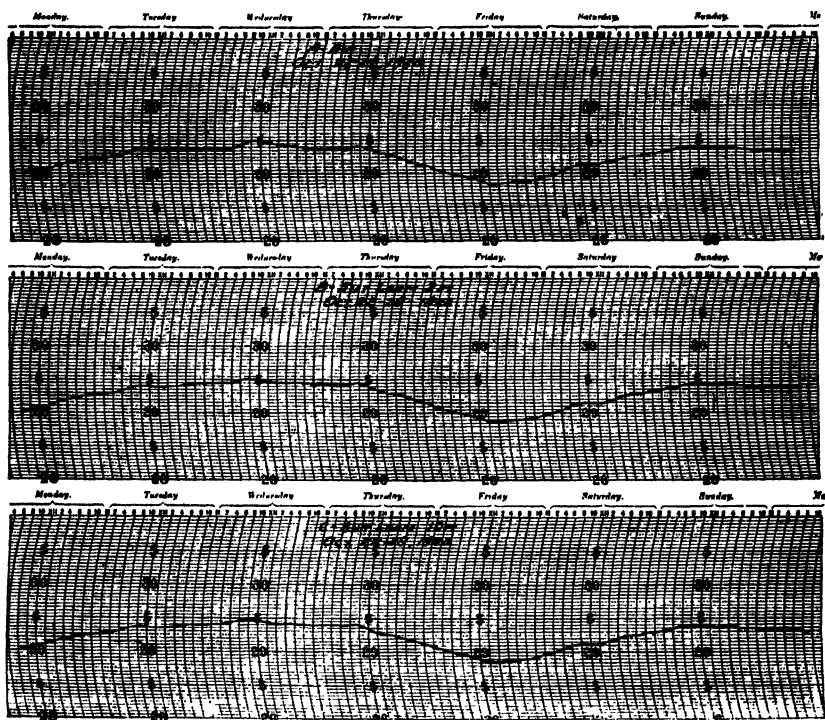
FIG. 3. DAILY MARCH OF BAROMETRIC PRESSURE IN AIR AND IN SILT LOAM AT DEPTHS OF 2 AND 10 FEET
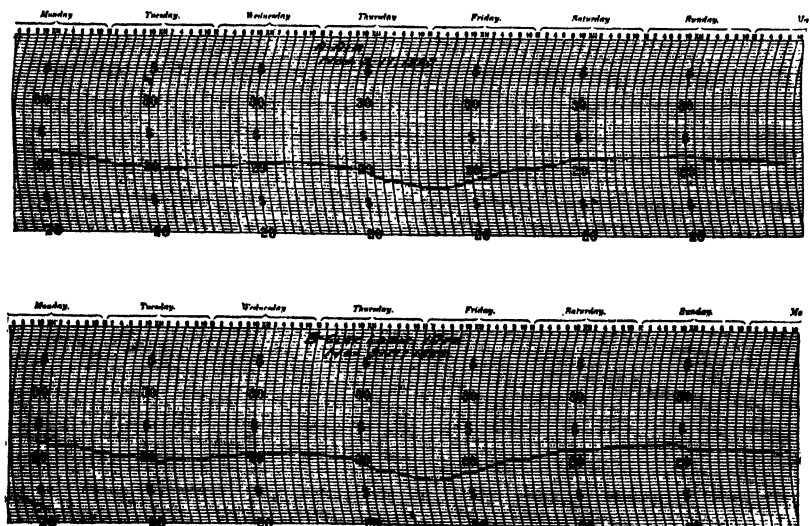
FIG. 4. DAILY MARCH OF BAROMETRIC PRESSURE IN AIR AND IN CLAY LOAM AT A DEPTH OF 10 FEET

variations of the outside pressure, but will lag somewhat behind them. For these reasons the depths of penetration and amounts of rinsing which we might compute by the method just described are only limiting maximum values which are never quite reached.
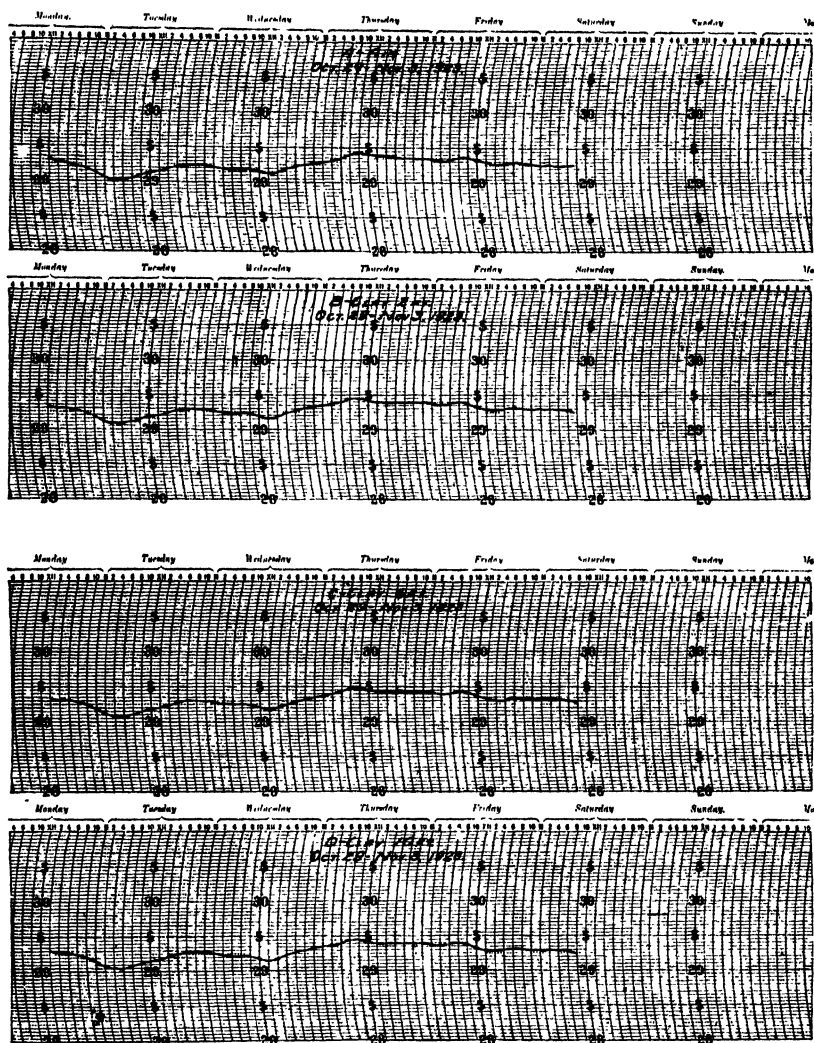
FIG. 5. DAILY MARCH OF BAROMETRIC PRESSURE IN AIR AND IN CLAY AT DEPTHS 2, 6 AND 10 FEET

From these and similar considerations Buckingham comes to the following conclusions as to the effect of barometric pressure or soil aeration.

Hence our ideal case of the inflow and outflow of the outside air with a sharp dividing surface between outside and soil air is a pure fiction. It does not correspond to the truth at all, and the rinsing which in the ideal case would be perfect once in each barometric oscilla-

tion down to the extreme depth of penetration of the wave is altogether unsignificant, though, of course, something of the sort does exist.

The experimental results obtained in this investigation do not seem to support the above statements and conclusions. On the contrary they seem to point strongly to the conclusion that atmospheric pressure changes must have an appreciable influence on soil aeration. Such a conclusion would seem reasonable and logical from the following facts. In the first place, since the barometric pressure in the soil is exactly the same as that in the air and that the variations that take place in the air occur also simultaneously in the soil, even to great depths, it would seem that the air can enter and leave the soil
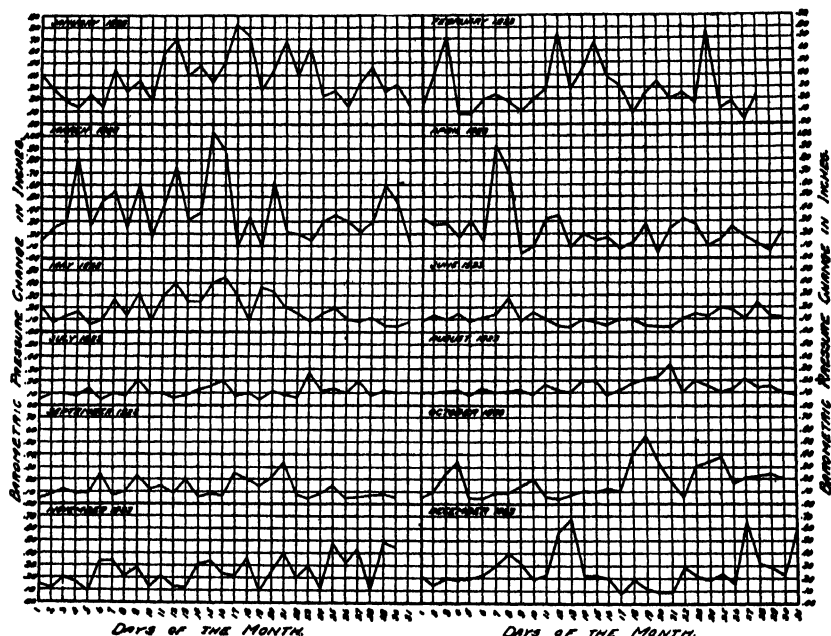
FIG. 6. DAILY MARCH OF AIR BAROMETRIC PRESSURE FOR THE YEAR 1923

with perfect freedom, and that it encounters no resistance in its free passage. In the second place, since the compressibility of air (gas) varies inversely as the pressure which it bears, it logically follows that as the barometric pressure of the atmosphere goes up the volume of the air already in the soil is diminished proportionally and more air is forced or compressed into the soil. Conversely, as the barometric pressure goes down the compression is released the volume increases and air goes out of the soil. By means of this change of barometric pressure the soil is aerated. Now the amount of aeration that the soil will receive in this way will depend first upon the extent of change of the barometric pressure, second upon the frequency of this change, and third upon the depth of soil filled with air. By referring to figures 1 to 6 inclusive,

the last showing the daily range of variation of the barometric pressure for the year 1923, an idea as to the magnitude of oscillation may be obtained. It will be readily seen that this factor varies considerably with the season. It is greatest in the fall, winter and spring months and lowest in the summer months. In the fall, winter and spring months it may be as great as 1 inch on some days and as low as 0.05 inch on others. But it is usually quite large during the colder seasons of the year. During the summer months, however, it is generally not very high. It may be as high as 0.5 inch on some days and as low as 0.02 inch on others, but usually it ranges around 0.10 and 0.20 inch.

From these data on the seasonal fluctuation of the barometric pressure it is evident that the soil receives its greatest aeration from this source during the colder seasons of the year, and the least during the warmer part of the year. This order would seem rather unfortunate, for the plants and the lower organisms perform their greatest activities during the warmer season and that is when the aeration is most needed. It must be remembered, however, that the foregoing daily fluctuations of barometric pressure refer to the latitude of the stations at which they were recorded. It is known that the daily amplitude varies considerably with the latitude, its greatest values being found in the equatorial regions, while the amount grows steadily less with the higher latitudes. An idea as to the difference of daily fluctuation of the barometric pressure at different latitudes may be obtained from the chart shown in figure 7 prepared by O. Farsig of United States Weather Bureau. It is evident from this chart that in the latitude of Mexico City the amplitude is comparatively large while that in Sitka, Alaska, it is very small. In the latitudes of South America the amplitude must be very large. The barometric pressure, therefore, must play a greater rôle in the aeration of soils in the southern than in the northern latitudes in both the warm and the cold parts of the year.

Long-time records show the following general characteristics as to the frequency of the daily variations of barometric pressure. The general tendency is for two maximum and two minimum pressures to occur every 24 hours. The chief maximum usually occurs at about 10 a.m., the chief minimum at 4 p.m., a secondary maximum at 10 p.m., and a secondary minimum at 4 a.m. The pressure is thus subject to a double oscillation in the course of a day. Whenever other meteorological elements do not interfere, these double maximum and minimum pressures will occur regularly in the course of the day. Hence, the soil may undergo two cycles of aeration each day.

It will now be of much interest and importance to ascertain the depth to which air will enter the soil when the barometric pressure rises to various degrees, and thus determine the depth of the soil directly aerated by the barometric pressure changes. Since the compressibility of the air is inversely proportional to the pressure, the depth of penetration for any degree of barometric rise will be proportional to the depth of the soil which is porous enough to allow free communication with the outside barometric pressure and is filled
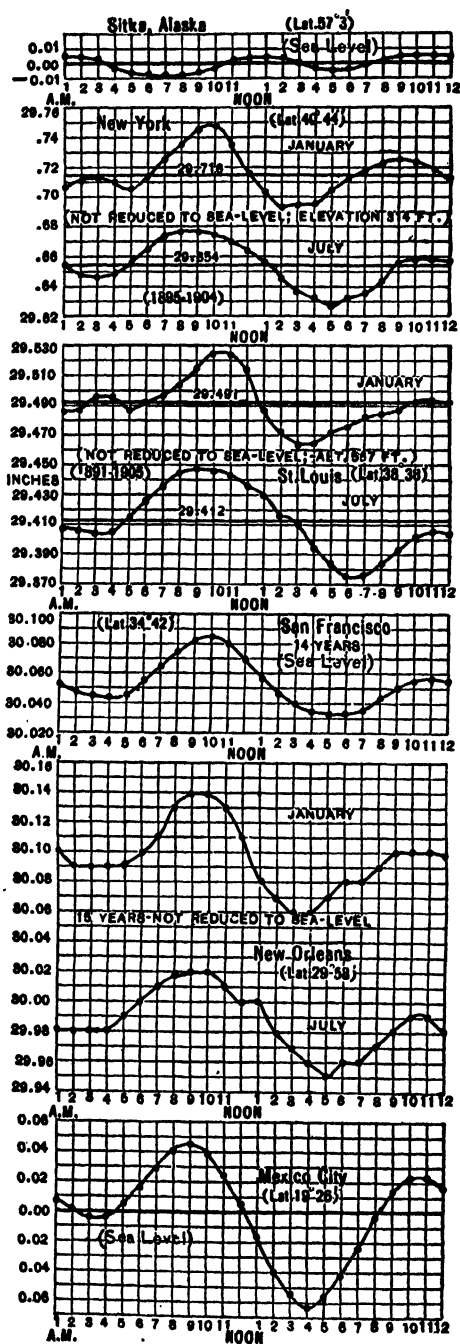
FIG. 7. DIFFERENCE IN DAILY VARIATION OF AIR BAROMETRIC PRESSURE AT DIFFERENT LATITUDES

with air. Normal soils should be porous or allow free communication of air to the water-table or to the zone of water saturation. A soil should be pervious to air that allows water to percolate and should be pervious to the depth that the water percolates, which is the water-table, or to some other impervious stratum. The depth of the water-table or impervious stratum must vary from a few inches to several hundred feet according to climate, topography and geology. If we assume that the impervious stratum is 100 feet and that the barometric pressure rises from 28.5· to 29.5 inches the degree to which air will be driven into the soil is 40.56 inches. This figure is obtained by multiplying the fractional rise of barometric pressure by the depth of the porous soil thus: $\frac{1}{29.5}$ x 100 = 3.39 feet, or 40.56 inches. In table 1 are shown the

TABLE 1

Depth of penetration of air into the soil as the barometric pressure and depth of soil vary

FRACTIONAL AMPLITUDE	DEPTH OF PENETRATION WHERE DEPTH OF SOIL IS			
	10 feet	25 feet	50 feet	100 feet
inch	inches	inches	inches	inches
0.1	0.4056	1.016	2.028	4.056
0.2	0.8112	2.232	4.056	8.112
0.3	1.2168	3.048	6.084	12.168
0.4	1.6224	4.064	8.112	16.224
0.5	2.0280	5.080	10.140	20.280
0.6	2.4336	6.096	12.168	24.336
0.7	2.8392	7.112	14.196	28.392
0.8	3.2448	8.128	16.224	32.448
0.9	3.6494	9.144	18.252	36.504
1.0	4.056	10.16	20.28	40.56

computed results on barometric wave penetration as the depth of the impervious stratum and the barometric pressure vary. A barometric pressure of 29.5 was taken as the standard in these calculations.

From these calculations it is seen that the depth of penetration of air into the soil varies from the extreme low of 0.4056 inch where the depth of the impervious stratum is only 10 feet and the barometric pressure rise 0.1 inch, to the extreme high of 40.56 inches where the depth of the impervious stratum is 100 feet and the barometric pressure rise 1 inch. The maximum extreme is doubtless exceeded in many regions of the earth where the daily fluctuations of the barometric pressure are more than an inch in certain seasons of the year. In the latitude of East Lansing, Michigan, the maximum daily fluctuation for 1923 was 0.88 inch in November and 1.05 inches in December, while the maximum monthly range was 1.52 inches in March. In the torrid zones and in some other regions the daily fluctuation may be considerably greater.

It is apparent, therefore, that when the amplitude of barometric pressure is high and the depth of the impervious stratum large the depth to which air will enter the soil is correspondingly very large. Conversely, when the magnitude of these two factors is low, the depth of penetration is correspondingly small. But for the average depth of soil and barometric pressure fluctuation the depth of penetration or aeration is quite appreciable and important. In the southern latitudes where the daily barometric fluctuations is very high, the depth of the air penetration must be very large.

It seems doubtful, however, if the full effects of barometric pressure changes on soil aeration are revealed by these calculated data on air-wave penetration. In the first place, the soil air close to the surface in composition is very much like the atmospheric air. When this upper soil air is pushed down by the rise of barometric pressure it brings about the same kind of aeration as the atmospheric air. The depth of the soil which receives this aeration is, therefore, greater than is shown in the calculation. In the second place, unevenness in topography, porosity, depth of impervious layer, etc., must cause considerable mixing up between the new and the old air. Finally, diffusion also must be considerably facilitated at the lower depths as newer air is driven down. All these and other benefits, therefore, are not revealed by the above calculation of air penetration or soil aeration. Hence, barometric pressure plays a much greater rôle on soil aeration than is commonly attributed to it.

Referring once more to the barographic charts, it becomes evident that since the barometric pressure is the same in the soil—even down to the depth of 10 feet—as that outside, the air enters and leaves the soil with perfect and instantaneous freedom. Such being the case, then, the current notion or practice of cultivating the surface soil in order to facilitate aeration, does not appear to have much foundation.

SUMMARY

In this paper are presented the results of an investigation on the aeration of soils as influenced by barometric pressure. The problem was studied by burying barographs in the soil and recording the march of the barometric pressure and comparing it with that in the air. It was found that the barometric pressure of the soil down to the depth of 10 feet was exactly the same as that in the air. Since this was true in all types of soil investigated including the heaviest clays, it seems reasonable to infer that the soil air has a free communication with the outside air down to the impervious stratum or watertable. Calculations show that when the amplitude of the barometric pressure is high and the depth of the impervious stratum large the amount of aeration or the depth to which new air will enter the soil, is correspondingly large. When these factors, however, are small in magnitude, the degree of penetration of air also is small. It seems, however, that barometric pressure has greater influence on soil aeration than is revealed by these calculations. But even

according to calculations the amount of aeration is quite appreciable and important for the average fluctuation and depth of impervious stratum. When the entire earth is taken into consideration the effect of barometric pressure on soil aeration is very large in some regions, especially in the torrid zones. From all evidences, it appears, therefore, that barometric pressure plays a greater rôle in soil aeration than is commonly attributed to it.

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SOIL SERIES AND TYPES FROM THE STANDPOINT OF HYDROGEN-ION CONCENTRATION AND LIME REQUIREMENT

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Under one designation or another differences in soil reaction have been long recognized and acted upon in practical agriculture. Fortunately in lieu of the somewhat vague and indefinite terms formerly used in discussions of this chemical characteristic of soils, there is at present wide acceptance among soil investigators of the physical-chemical conception of acidity and alkalinity. Soils are acid, alkaline, or neutral, when in their respective soil solutions there is a concentration of hydrogen ions greater than, less than, or equal to the concentration of hydroxyl ions.

Reports resulting from systematically undertaken field observations on the part of Wherry (19), Kelley (14), Olsen (15) and others, emphasize hydrogen-ion concentration of the soil solution as one very potent factor among those which determine the distribution of natural plant species. Likewise research in the field of plant nutrition by Hoagland (11), Joffe (12), Fred and Davenport (6), Bryan (3, 4, 5) and others, affords very fundamental reasons for differences of procedure that prevail in soil management and crop production in everyday farm practice. A fair conclusion from researches in this field at present is that some crops are most exacting, others less so, in the matter of intensity of reaction in soil solutions from which they obtain elements of nutrition. Their requirements in this particular must be met in the interests of maximum production.

Within certain limits of hydrogen-ion concentration, a wide range of extensively used cultivated crops is annually produced the world over. In soils whose hydrogen-ion concentration lies beyond either limit it becomes increasingly difficult to grow the generally recognized useful crops. There is expended annually in various parts of the United States alone an enormous amount of capital and energy in maintaining in cultivated soils a desirable intensity of reaction for this or that crop and in attempts to change the intensity of reaction in waste lands to such an extent that they, too, may become profitably productive. In practical agriculture it is highly important for one to know within limits the intensity of reaction of that soil in which he is financially or otherwise interested.

OBJECTIVES IN HYDROGEN-ION DETERMINATIONS

In comparison with some other determinations that are commonly involved in soil investigations the number of hydrogen-ion determinations is not large. From available records of those in print it appears that they have been undertaken with one or more of five objectives: (a) To ascertain merely if one might properly speak of soils as having a hydrogen-ion concentration. As already intimated that inquiry has been answered decisively in the affirmative. (b) To ascertain within what limits of hydrogen-ion concentration extensive areas of cultivated soils might fall. Thus Sharp and Hoagland (18) report for California soils a hydrogen-ion concentration, expressed in pH values, ranging between 3.7 and 9.7; Plummer (16), for North Carolina soils, reports the extreme limits pH 4.04 and pH 9.68; and Olsen (15) for Danish soils, pH values between 3.4 and 8.0. (c) To note any correlation that might prevail between the soil's hydrogen-ion concentration and its lime requirement as determined more particularly by the Veitch method. Blair and Prince (2) appear to be reasonably sure of a fairly close correlation in this regard from their determinations on soils of certain rotation plats of the New Jersey Experiment Station. Johnson (13), from a much more extended study of soil types, sees at the best nothing approaching close correlation. (d) To ascertain if well defined series and soil types have a characteristic hydrogen-ion concentration. Gillespie and Hurst (7, 8) show for two soil types in Maine fairly consistent data in support of that view, and correlate the greater hydrogen-ion concentration of one type, Caribou loam, with comparative freedom from scab of potatoes grown in it. Kelley (14), from field observations in Pennsylvania on native plant species, feels justified in assigning an average pH value to each of seven soil types studied. (e) To ascertain if procedures by the colorimetric method and by use of the hydrogen electrode are productive of reasonably close agreement in hydrogen-ion concentration values. Gillespie and Hurst (7, 8) offer perhaps the most conclusive evidence thus far that such is the case, provided the relative amounts of soil and water in the two procedures are the same.

OBJECTIVES IN THIS WORK

At the Oregon Experiment Station a great deal of research work of one kind or another centers quite definitely around soil series and types. One prominent activity on the part of the Experiment Station for several years has been cooperation with the Bureau of Soils, United States Department of Agriculture, in soil surveys of the several counties which together make up the area known on the Pacific Coast as the Willamette Valley. The soils of the entire valley are acid in reaction. This fact is noteworthy because there are comparatively few extensive areas of acid soils in the Inter-Mountain and Pacific Northwest states. They occur mostly in the regions of high rainfall west of the Cascade Range of Mountains. The valley has an extremely interesting geological history.

The mapping of soil types by field parties is followed closely by chemical analyses that establish very valuable sources of information for those who are conducting investigations in fertilizer requirements and for others engaged in farming operations.   The completion of the survey for Benton County, home of the State Agricultural College and Central Experiment Station, suggested the following chemical work in addition to that usually undertaken in our study of soil types.   Three considerations appeared to warrant the extra work involved:

(*a*) If intensity of soil reaction in a large measure determines the cropping system one must follow, it is highly advantageous to know whether this or that series and type of soil, wherever encountered, exhibits as definite characteristics in the matter of reaction as from the standpoint of comparative richness in plant-food elements.

(*b*) The growth of one or more kinds of legumes is as fundamental to permanent productivity here as elsewhere.   This series of determinations promised explanations of a fundamental nature for the correlation of soil series and types with field observations on their ability to promote the growth of this or that legume.

(*c*) There would be established additional data by which to judge whether any definite relationship prevails between the intensity of a soil's reaction and that soil's lime requirement.   It is believed that liming practice—not extensive as yet—can be established eventually on a better understanding of legume and other crop lime requirements.

FIELD WORK

The taking of samples required three days of travel during the early summer of 1923. The soil survey map was carried on the sampling trips to serve as a guide in the location of the several areas of any one type.   It is a very "spotted" map; for the areas that together make up the total acreage of any one type in many instances are separated by intervening areas of other types varying in width from a few rods to several miles.   Eleven of the most prominent series under cultivation are each represented by one or two types.   Samples were taken of the surface soils only to a depth of approximately 8 inches.   No area gone over is represented by less than two samples.   In the laboratory the samples were air-dried, sifted through a coarse screen, and stored in Mason fruit jars for the analytical work.

DETERMINATION OF HYDROGEN-ION CONCENTRATIONS

Previous to sampling it was intended to make determinations of hydrogen-ion concentration by colorimetric procedure.   Two weeks or more were spent in attempts to perfect a satisfactory procedure, with an experience and results almost identical with those related by Gimingham (9).   The hydrogen electrode was then brought into use with results that were highly satisfactory.   An

equipment similar to that described by Hildebrand (10) was employed. The "null" point was determined with a galvanometer and voltage with a millivolt-meter. Voltages were converted to corresponding pH values by use of the table published by Schmidt and Hoagland (17).

For these determinations the soils were made to pass a 60-mesh sieve by rubbing with a wide rubber stopper. Occasionally some light rubbing in a mortar was a necessary preliminary. Five grams in duplicate were then placed with 10 cc. of water in small bottles and agitated for 30 minutes with a mechanical shaker. Thus treated in the late afternoon the samples were allowed to stand over night. The determination of hydrogen-ion concentration was completed the following day.

In most instances equilibrium with the hydrogen electrode was attained within one-half or three-quarters of an hour. Now and then as much as two hours were required to secure constant readings of voltage. In attaining equilibrium no one series or type exhibited any definite characteristic in the matter of time. It is quite probable that with better agitation of the soil suspension than could be secured with the hydrogen stream alone, greater uniformity in the matter of time would have been noted. The platinum electrodes were frequently recoated with platinum black, and check readings were frequently made on solutions of known pH values.

The lime requirement was made by the Albert method as perfected by Bizzell and Lyon (1). It will be noticed that a number of determinations were also made by the Veitch method. Excepting the Newberg series, results by the two methods are in as close agreement as one might reasonably expect.

GROUPING OF SERIES

In the tabulation of analytical data the grouping of series adopted in soil survey work for the entire valley was followed.

Olympic, Aiken, Melbourne and Carlton are residual soils. The first two are derived from basaltic rocks and are known locally as red hill lands. The last two are derived from sedimentary shales and sandstones. Melbourne is reddish brown in color. On it are located some of the most thrifty orchards of Benton County. Carlton is greyish-brown on a grey mottled subsoil indicative of poor drainage.

Willamette, Dayton and Amity, with other series not represented here, make up a class called "Old Valley Filling Soils." Dayton (whiteland) is always imperfectly drained, and Amity is frequently found in that condition.

Newberg and Chehalis are first and second bottom lands respectively of more recently made soils. They are overflowed annually by the Willamette River, but quickly recover a well drained condition. Wapato is a low, poorly drained soil adjacent to creeks. Cove Clay is a poorly drained Adobe almost unworkable when it becomes the least bit dry.

TABLE 1

Analytical data on hydrogen-ion concentration and lime requirement by series and types

Results tabulated are averages of closely agreeing duplicate determinations

SERIES AND TYPE	SOIL NUMBER	HYDROGEN-ION CONCENTRATION 5 GM. SOIL 10 CC. H_2O	LIME REQUIREMENT CaO PER 2,000,000 POUNDS OF SOIL	
			Albert method	Veitch method
		pH	*pounds*	*pounds*
Residual soils:				
Olympic: Silty clay loam	1	5.63	2,038	
	2	5.22	2,654	2,600
Aiken: Silty clay loam	1	6.15	2,374	
Melbourne Silt loam	1	4.63	3,304	3,600
	2	4.72	4,637	
	3	5.48	2,744	
	4	5.28	1,972	
	5	5.71	2,151	
	6	5.74	2,151	
	7	4.94	4,614	
	8	5.44	2,654	
	9	5.08	2,442	
	10	5.44	1,691	
	11	5.61	1,904	1,600
Clay loam	1	5.01	2,856	
	2	5.12	4,602	
	3	5.22	3,730	
	4	5.35	3,192	
	5	5.11	2,777	3,000
	6	5.31	2,509	
Carlton: Silt loam	1	5.53	2,285	
	2	5.99	2,038	1,200
	3	5.39	2,621	
	4	5.41	3,304	
	5	5.59	3,550	3,400
Old Valley Filling—mixed material:				
Willamette: Clay loam	1	4.78	3,707	3,600
	2	4.63	3,360	
	3	5.53	1,915	
	4	5.53	2,028	
	5	5.65	2,576	
	6	5.62	2,554	
	7	5.15	2,755	
	8	5.28	2,576	
	9	5.73	2,442	2,200

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TABLE 1—*Continued*

SERIES AND TYPE	SOIL NUMBER	HYDROGEN-ION CONCENTRATION 5 GM. SOIL 10 CC. H₂O	LIME REQUIREMENT CaO PER 2,000,000 POUNDS OF SOIL	
			Albert method	Veitch method
		pH	*pounds*	*pounds*
Dayton: Silty clay loam........................	1	4.80	2,004	1,800
	2	4.80	2,401	
	3	4.89	2,285	
	4	4.81	2,789	
	5	5.03	2,576	
	6	5.33	2,553	
	7	5.12	2,330	
Amity: Silty clay loam.........................	1	5.88	2,565	
	2	5.14	3,718	
	3	5.47	2,213	
	4	5.41	2,532	2,000
	5	5.56	3,517	
	6	5.66	2,867	
	7	5.21	2,990	
	8	5.28	2,688	
	9	5.41	3,046	2,800
	10	5.44	2,284	

Recent soils—Alluvial:

SERIES AND TYPE		SOIL NUMBER	HYDROGEN-ION CONCENTRATION 5 GM. SOIL 10 CC. H₂O	Albert method	Veitch method
Chehalis	Clay loam.........................	1	6.10	1,904	
		2	6.19	2,004	
		3	6.09	2,027	1,800
		4	6.17	2,072	
		5	6.20	1,745	1,400
		6	5.94	2,173	1,800
		7	6.08	1,781	
		8	6.02	2,240	
	Silty clay loam.....................	1	6.17	2,027	1,600
		2	6.14	1,546	
		3	6.15	2,060	
		4	5.68	2,677	
		5	5.73	2,722	2,800
Newberg: Silt loam...........................		1	6.06	1,422	600
		2	6.57	2,386	
		3	6.15	2,240	200
		4	6.15	2,285	
		5	5.76	2,621	

TABLE 1—*Continued*

SERIES AND TYPE	SOIL NUMBER	HYDROGEN-ION CONCEN-TRATION 5 GM. SOIL 10 CC. H₂O	LIME REQUIREMENT CaO PER 2,000,000 POUNDS OF SOIL	
			Albert method	Veitch method
		pH	*pounds*	*pounds*
Newberg: Silty clay loam	1	6.93	3,002	
	2	6.91	2,284	
	3	6.15	1,770	
	4	5.88	2,350	1,200
	5	6.10	2,733	
	6	7.40	1,624	
Wapato: Silty clay loam	1	4.53	4,838	4,440
	2	4.92	5,320	4,200
	3	4.67	5,958	
	4	5.05	4,722	
	5	4.63	7,000	
	6	5.01	2,867	
	7	5.20	3,908	
	8	4.62	4,368	
	9	4.63	3,618	
Cove: Clay	1	5.56	3,864	
	2	5.65	3,450	3,000
	3	5.52	3,058	
	4	5.48	2,755	

COMMENTS ON TABULATED DATA

Hydrogen-ion concentration

From a study of analytical data in table 1, it is apparent that in series and types there are marked differences in hydrogen-ion concentration. From a number of types samples can be picked whose active acidity is approximately ten times that of other samples representative of the same type. With most types, however, it is also apparent that if one or two samples, representing perhaps for the type extremes in active acidity, were to be discarded, there would appear a remarkable uniformity in hydrogen-ion concentration for the remaining samples. Illustrative of this fact is the Dayton Silty Clay Loam and the Willamette Clay Loam. Chehalis Clay Loam stands out prominently in its uniformity of hydrogen-ion concentration.

When the data are condensed as in table 2 a grouping of all series and types from the standpoint of hydrogen-ion concentration is possible under one of three classes. Dayton and Wapato are unquestionably the most intensely acid; Chehalis, Newberg and Aiken are least so; all others stand between the extremes but as a rule much closer to the more intensely acid ones. The

grouping here is not identical with that which is based on the geological mode of formation. In this connection note should be taken of the fact that two series in the group whose types here show least active acidity, wherever found, are rich in calcium. Their percentage ranges from 2 to 3, whereas the calcium content of all other series represented here is more frequently found to be well under 1 per cent than even slightly over. In the light of these analytical data it seems fair to state that these series and types are as definitely characterized by their hydrogen-ion concentration as by any other one chemical property.

TABLE 2

Summarized analytical data plus percentages indicative of calcium content from other analyses

SERIES AND TYPE	NUMBER OF SOILS	HYDROGEN-ION CONCENTRATION			CALCIUM Ca	LIME REQUIREMENT CaO PER 2,000,000 POUNDS OF SOIL		
		Maxi- mum	Mini- mum	Aver- age	Per cent	Maxi- mum	Mini- mum	Aver- age
		pH	*pH*	*pH*		*pounds*	*pounds*	*pounds*
Dayton: Silty clay loam........	7	4.80	5.33	4.98	0.33	2,789	2,004	2,494
Wapato: Silty clay loam........	9	4.53	5.20	4.81	0.89	7,000	2,867	4,677
Willamette: Clay loam.........	9	4.63	5.73	5.32	0.85	3,707	1,915	2,657
Amity: Silty clay loam........	10	5.14	5.88	5.45	0.90	3,718	2,213	2,842
Carlton: Silt loam..............	5	5.39	5.99	5.45	0.65	3,550	2,038	2,760
Melbourne:								
Silt loam...................	11	4.63	5.74	5.28	0.62	4,637	1,691	2,751
Clay loam..................	6	5.01	5.35	5.19	0.31	4,602	2,509	3,277
Olympic: Silty clay loam.......	2	5.22	5.63	5.43	0.69	2,654	2,038	2,346
Cove: Clay...................	4	5.48	5.65	5.55		3,864	2,755	3,282
Aiken: Silty clay loam.........	1			6.15	0.36			2,374
Chehalis:								
Clay loam..................	8	5.94	6.20	6.10	2.09	2,240	1,745	1,993
Silty clay loam.............	5	5.68	6.17	5.97	2.49	2,722	1,546	2,206
Newberg:								
Silt loam...................	5	5.76	6.57	6.14	2.92	2,621	1,422	2,191
Silty clay loam.............	6	5.88	7.40	6.56	2.67	3,002	1,624	2,291

Correlation with field observations

The second consideration in this work is the possible correlation of field observations on the relative ease with which various legumes, climatically adapted to the Pacific Northwest, can be grown on these series, with data that are representative of their hydrogen-ion concentration or intensity of reaction.

Soil survey parties whose observations are the most extensive, rule out alfalfa production as a practicable possibility on all series represented here excepting Newberg and Chehalis. Red clover gets no recommendation for Dayton and Wapato series. Very frequently it does not grow thriftily on the types intermediate between those of greatest and those of least intensity of

acidity. This fact is taken to be indicative of an intensity of acidity in those types that is almost the limit of tolerance for red clover. Common and Hungarian vetches thrive on any of the series with the possible exception of very poorly drained areas of Dayton and Wapato. No series appears to be too intensely acid for alsike clover. These correlations with field observations are necessarily crude. It will be noticed at once, however, that in so far as alfalfa, red clover and alsike clover are concerned they check deductions drawn from results of solution and pot culture tests on the part of other investigators. The interesting and important agronomic fact is the outstanding ability of the vetches to thrive under conditions of acidity that are discouraging, if not forbidding, to alfalfa and red clover.

Lime requirement

From the assembled data in table 1, it is apparent that these soil series do not lend themselves to any grouping that would be illustrative of a fundamental connection between hydrogen-ion concentration and lime requirement. It may be said that those series which show the least intensity of acidity, Newberg and Chehalis, have a relatively low lime requirement. On the other hand, one only, of the two most intensely acid series, has a correspondingly high lime requirement. Melbourne Silt Loam is the only type within which lime requirement rises or falls in rough agreement with the increase or decrease in hydrogen-ion concentration. On the whole, this work answers in the negative the query as to correlation between the intensity of a soil's reaction and its lime requirement.

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A COMPARISON OF SEVERAL QUALITATIVE TESTS FOR SOIL ACIDITY

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Although many qualitative tests for soil acidity have been developed during the past few years and satisfactory results have been obtained in some cases, there is still some doubt as to the accuracy of the various methods, when used under certain conditions. Hence it has seemed desirable to study several of the more important methods and to ascertain if possible which tests are best suited for the determination of soil acidity in the field.

For a field test accuracy, simplicity and rapidity are essential. With these factors in mind, a large number of observations were made with various tests on 51 soils secured as follows; 17 from Prof. E. Truog, Wisconsin; 14 from Prof. E. E. DeTurk, Illinois; 6 from Prof. F. L. Duley, Missouri; and the remaining number from various parts of Iowa. The samples were all air-dried, ground to pass a 20-mesh sieve, and tested by the following methods:

1. Hydrogen-ion concentration. Determined electrometrically on a suspension made by shaking 50 gm. of soil and 100 cc. of distilled water in an Erlenmeyer flask for 20 minutes.

2. "Soiltex." Made as recommended by Spurway (9).

3. Truog test. Made as recommended by Truog (10).

4. Comber potassium thiocyanate test. Made by placing 5 gm. of soil and 10 cc. of 95 per cent ethyl alcohol containing 4 per cent of potassium thiocyanate in a 20 by 150-mm. test tube (1). Tube stoppered, shaken 30 seconds and centrifuged 1 minute to secure a clear solution for comparison.

5. Comber potassium salicylate test. Same as the previous test except that a water solution containing 5 per cent of potassium salicylate was used in place of the alcoholic solution of potassium thiocyanate (2).

6. "Richorpoor." A modification of the Comber potassium thiocyanate test, a different solvent being used. Made as in no. 4, with the Richorpoor solution in place of the alcoholic solution of potassium thiocyanate.

7. "The Iowa Test." Developed by Emerson (4), also a modification of the Comber potassium thiocyanate test, a different solvent being used. Distinctive in that it includes a saturated solution of neutral ammonium molybdate in ether which is used when moist soils are being tested.

The LaMotte indicator field set, as recommended by Wherry (11) was tried in connection with this study, but with most soils too much time was required to secure a clear soil extract. This was considered very objectionable since rapidity is one of the essentials of a field test; consequently the results were not included.

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TABLE 1

Comparison of qualitative tests for soil acidity made on dry soils and hydrogen ion concentration of soil suspensions expressed in terms of pH values

NUMBER	SOIL TYPE	SOURCE	pH VALUE	SOLTEX	TRUOG TEST	COMBER POTASSIUM THIOCYANATE	COMBER POTASSIUM SALICYLATE	RICHORFOOR	IOWA TEST
1	Gray silt loam	Odin, Ill.	4.60	st.*	st.	st.	st.	st.	st.
2	Yellow gray silt loam	Raleigh, Ill.	4.80	st.	v.st	st.	st.	v.st.	st.
3	Marion silt loam	Unionville, Iowa	4.90	st.	v.st.	v.st.	v.st.	v.st.	v.st.
4	Brown silt loam (loess)	Illinois	4.90	st.	st.	med.	st.	st.	st.
5	Raw peat	Manistique, Mich.	4.90	c.n.b.r.	v.st.	v.v.st.	v.st.	v.st.	v.st.
6	Waverly silt loam	Boone Co., Mo.	4.95	st.	v.st.	v.st.	v.st.	v.v.st.	v.v.st.
7	Yellow gray silt loam†	Raleigh, Ill.	4.95	st.	v.st.	st.	st.	v.st.	v.st.
8	Grundy silt loam	Mt. Pleasant, Iowa	5.00	st.	st.	st.	st.	st.	st.
9	Marion silt loam	Boone Co., Mo.	5.05	st.	st.	st.	st.	st.	st.
10	Waukesha silt loam	LaCrosse Co., Wis.	5.25	med.	st.	st.	v.st.	st.	med.
11	Decomposed peat	Manito, Ill.	5.25	st.	med.+	n.a.	v.st.	sl.	sl.
12	Carrington sand	Vinton, Iowa	5.35	st.	med.+	med.	sl.	med.	st.
13	Carrington loam	Calamus, Iowa	5.40	st.	st.	med.	med.	med.	st.
14	Brown silt loam	Bloomington, Ill.	5.45	st.	med.+	sl.	st.	sl.	med.
15	Brown silt loam†	Bloomington, Ill.	5.45	st.	med +	med.	st.	med.	st.
16	Carrington loam	Independence, Iowa	5.50	st.	st.	st.	st.	st.	st.
17	Carrington silt loam	Springlvie, Iowa	5.50	st.	st.	st.	v.st:	st.	st.
18	Clyde silt loam	Union Grove, Wis.	5.50	med.	st.	med.	med.	med.	st.
19	Dune sand	Oquawka, Ill.	5.55	st.	med.	n.a.	sl.	n.a.	n.a.
20	Yellow silt loam†	Elizabethtown, Ill.	5.60	st.	med.	med.	med.	med.	st.
21	Waukesha silt loam	Galesville, Wis.	5.60	med.	med.	med.	med.	med.	med.
22	Buckner coarse sand	Muscatine, Iowa	5.60	st.	st.	med.	med.	sl.	sl.
23	Tama silt loam	State Center, Iowa	5.80	med.	st.	st.	st.	st.	st.

No.	Soil	Location	pH value						
24	Red sandy loam	Georgia	5.90	med.	med.	n.a.	sl.	n.a.	med.
25	Shelby loam	Jamison, Iowa	5.90	med.	med.	sl.	sl.	sl.	med.
26	Miami silt loam	Sun Prairie, Wis.	5.90	med.	med.	med.	med.	sl.	med.
27	Shelby loam	Udell, Iowa	5.95	st.	st.	med.	st.	sl.	med.
28	Clarksville gravelly loam	Lawrence Co., Mo.	5.95	med.	sl.+	n.a.	sl.	n.a.	n.a.
29	Yellow silt loam	Elizabethtown, Ill.	5.95	st.	sl.	n.a.	sl.	sl.	sl.
30	Miami silt loam	Burlington, Wis.	5.95	med.	sl.+	sl.	sl.	sl.	sl.
31	Lintonia sand	Mississippi Co., Mo.	6.00	st.	sl.+	n.a.	n.a.	n.a.	n.a.
32	Miami silt loam	Stoughton, Wis.	6.05	med.	sl.+	sl.	med.	sl.	med.
33	Waukesha silt loam	Mazomanie, Wis.	6.00	med.	med.	v.st.	v.st.	v.st.	v.st.
34	Miami fine sandy loam	Racine Co., Wis.	6.05	med.	sl.+	sl.	sl.	sl.	med.
35	Miami silt loam	Franksville, Wis.	6.05	med.	sl.+	sl.	sl.	sl.	med.
36	Huntington silt loam	Hickory Co., Mo.	6.15	med.	sl.+	sl.	sl.	n.a.	sl.
37	Marshall silt loam	Missouri Valley, Iowa	6.25	med.	med.	sl.	sl.	sl.	sl.
38	Baxter gravelly loam	Polk Co., Mo.	6.30	med.	sl.	n.a.	sl.	n.a.	n.a.
39	Carrington silty clay	Union Grove, Wis.	6.50	sl.	sl.+	n.a.	sl.	n.a.	sl.
40	Miami fine sandy loam	Racine Co., Wis.	6.55	med.	sl.+	n.a.	sl.	n.a.	sl.
41	Gray silt loam†	Odin. Ill	6.65	sl.	sl+	med.	med.	n.a.	med.
42	Caledonia, Wis.	Caledonia, Wis.	6.70	sl.	sl.+	n.a.	med.	n.a.	sl.
43	Carrington silt loam	Jamison, Iowa	6.80	sl.	sl.+	sl.	sl.	n.a.	med.
44	Shelby loam	LaCrosse Co., Wis.	6.80	neut.	sl.+	n.a.	n.a.	n.a.	sl.
45	Waukesha silt loam	Rochester, Wis.	7.90	sl.	sl.	n.a.	n.a.	n.a.	n.a.
46	Miami silt loam	Hartsburg, Ill.	7.95	neut.	sl.	n.a.	n.a.	n.a.	n.a.
47	Black clay loam	Stoughton, Wis.	8.00	alk.	n.a.	n.a.	n.a.	n.a.	n.a.
48	Decomposed peat	Ames, Iowa	8.20	sl.	n.a.	n.a.	n.a.	n.a.	n.a.
49	Webster silty clay loam	Hartsburg, Ill.	8.55	alk.	sl.	n.a.	n.a.	n.a.	n.a.
50	Black clay loam†	Burlington, Wis.	8.55	alk.	n.a.	n.a.	n.a.	n.a.	n.a.
51	Clyde silty clay	Missouri Valley, Iowa	8.75	alk.	n.a.	n.a.	n.a.	n.a.	n.a.

*st., strong; sl., slight; v., very; n.a., not acid; c.n.b.r., could not be read; med., medium; alk., alkaline; neut., neutral.

†Subsoil.

The method of expressing acidity as recommended by Truog (10) has been followed. In case of "Soiltex" which also differentiates between neutral and basic (alkaline) soils, the nomenclature as given on the Soiltex reaction chart has been used.

The results of the various tests were all made comparable by calling the colors produced by the different tests on soil 1, table 1, strongly acid. All of the other soils were classified according to the amount of color which developed when each of the various tests was used. The data are given in table 1.

A fairly good agreement was secured with all of the tests except in the case of the sandy soils and the acid peats. Soil 5, which is a raw acid peat, would not mix with the Soiltex solution and the acidity could not be determined. Even after the peat had been moistened for several days the test could not be used. Where clear solutions could be obtained, the Soiltex results agreed fairly well with the hydrogen-ion concentration. Very strongly acid soils could not be differentiated from strongly acid soils as indicated by the Soiltex reaction chart. In this test clear solutions are absolutely essential for correct results. Slight turbidity is quite difficult to prevent in clay soils, and in case of heavy dark colored soils, turbidity may darken the color of the solution to such an extent that the soil will appear much less acid than it would if the extract were perfectly clear.

The results secured by the Truog test do not agree quite as well with the hydrogen-ion concentration of the soil suspensions as Soiltex. This is due to the fact that the two tests measure different kinds of acidity. The Soiltex test depends upon the concentration of hydrogen ions in the soil solution which may be considered as the intensity of the acidity. The Truog test measures total acidity, which in some soils may be low but of high intensity; or in other cases, the amount of acidity may be large and the intensity low. For this reason these two methods would not be expected always to give the same results.

The last four methods do not measure soil acidity but measure easily replaceable iron. Comber (1) states, "The color cannot be used as a comparative measure of the lime requirement of different soils; for only iron is identified in this test in a mixture of iron and aluminum which will vary from one soil to another." Carr (3) has attempted to make the method quantitative by titrating the alcoholic potassium thiocyanate extract with standard sodium hydroxide, since both aluminum and ferric hydroxide are completely precipitated when the pH value of the solution is raised above 5.5. This procedure could not be used in the field.

A study of table 1 indicates that the amount of replaceable iron has a relation to soil acidity; and in loams, silt loams and heavier soils, the results secured by tests measuring replaceable iron compare quite favorably with the hydrogen-ion concentration of the soil suspensions. In the case of sandy soils the results were low. In case of soil 33 the results were much too high as compared with the other methods. A further study is being made on this soil.

The Comber potassium salicylate test required much more time than the other tests measuring replaceable iron, because soil colloids settle more slowly in water than in organic solutions. Potassium salicylate cannot be used in other solvents such as acetone which would hasten the rate of settling of the soil because ferric salicylate does not produce nearly as much color in organic solvents as in water.

The Comber potassium thiocyanate and Richorpoor tests gave about the same results. The soils used in this study settled more slowly in these solutions than in the Iowa test solution no. 2, and it was also found that the Iowa test was more sensitive than the Comber and Richorpoor tests giving a light red color in slightly acid soils, a scarlet color in medium acid soils and a dark red color in strongly acid soils.

Comber (1) has noted that the use of an ether-alcohol mixture increased the sensitivity of the potassium thiocyanate test. An acetone solution of potassium thiocyanate dissolves more iron from a soil than the same amount of potassium thiocyanate in either methyl or ethyl alcohol. The addition of ether to the acetone solution of potassium thiocyanate causes a further increase in the amount of iron dissolved. Carr (3) has shown that the acidity of the alcoholic potassium thiocyanate solution was an important factor in the amount of iron extracted from a soil. His results were confirmed in the case of methyl and ethyl alcohol, but it was found that acidity was not important in the case of acetone solutions. When 0.1 cc. of glacial acetic acid and 10 cc. of an alcoholic solution of potassium thiocyanate were added to 5 gm. of a slightly acid soil and shaken, a dark red color was produced. Only a light pink color was secured when the acid was not added. When the same amount of acetic acid was added to 10 cc. of acetone containing 1 per cent of potassium thiocyanate, and shaken with 5 gm. of the same soil, no increase in color was produced over that of a solution of potassium thiocyanate in acetone containing no acid.

EFFECT OF MOISTURE ON ACIDITY TESTS

An accurate field test for soil acidity should give the same results on either moist or dry soils. In the previous experiment only dry soils were used. In this experiment both moist and dry soils were studied under the various methods as given in table 1.

Emerson (4) has recommended the addition of a saturated solution of neutral ammonium molybdate in ether to moist soils before adding the solution containing the potassium thiocyanate. In order to determine how much the different tests were affected by moisture, 12 acid soils and 2 acid peats were selected. Twenty cubic centimeters of distilled water were slowly added to 100 gm. of dry soil. The mass was thoroughly mixed, covered and allowed to stand over night. The water content of the peats was made up in a similar manner to 100 and 200 per cent, respectively. Equivalent amounts of soil

Effect of moisture on qualitative tests for soil acidity

NUMBER	SOIL AND SOURCE	H₂O CONTENT	SOILTEX	TRUOG TEST	COMBER POTASSIUM THIOCYANATE	COMBER POTASSIUM SALICYLATE	RICHORPFOOR	IOWA TEST*
		per cent						
1	Brown silt loam; Bloomington, Ill.	none	st.†	med.+	sl.	st.	sl.	st.
2	Brown silt loam; Bloomington, Ill.	20	st.	med.+	n.a.	st.	n.a.	v.st.
3	Gray silt loam; Odin, Ill.	none	st.	st.	v.st.	st.	st.	st.
4	Gray silt loam; Odin, Ill.	20	st.	st.	st.	st.	st.	v.st.
5	Yellow gray silt loam; Raleigh, Ill.	none	st.	v.st.	st.	st.	v.st.	st.
6	Yellow gray silt loam; Raleigh, Ill.	20	st.	v.st.	st.	st.	v.st.	v.st.
7	Muck; Manito, Ill.	none	med.	med.+	n.a.	v.st.	sl.	med.
8	Muck; Manito, Ill.	100	d.t.r.	med.+	n.a.	v.st.	n.a.	st.
9	Clyde silt loam; Union Grove, Wis.	none	st.	st.	med.	st.	med.	st.
10	Clyde silt loam; Union Grove, Wis.	20	st.	st.	med.	st.	sl.	v.st.
11	Waukesha silt loam; Mazomanie, Wis.	none	st.	med.	st.	v.st.	v.st.	v.st.
12	Waukesha silt loam; Mazomanie, Wis.	20	st.	med.	st.	v.st.	sl.	st.
13	Marion silt loam; Boone Co., Mo.	none	st.	st.	med.	st.	st.	st.
14	Marion silt loam; Boone Co., Mo.	20	st.	st.	med.	st.	med.	st.
15	Waverly silt loam; Boone Co., Mo.	none	st.	v.st.	v.st.	v.st.	v.v.st.	v.v.st.
16	Waverly silt loam; Boone Co., Mo.	20	st.	v.st.	v.st.	v.st.	v.v.st.	v.v.st.
17	Carrington silt loam; Springville, Ia.	none	st.	st.	st.	v.st.	st.	st.
18	Carrington silt loam; Springville, Ia.	20	st.	st.	med.	v.st.	st.	v.st.
19	Carrington sand; Vinton, Iowa.	none	st.	med.+	med.	sl.	med.	med.
20	Carrington sand; Vinton, Iowa.	20	st.	med.+	med.	sl.	med.	med.
21	Tama silt loam; State Center, Iowa.	none	st.	med.	st.	st.	st.	st.
22	Tama silt loam; State Center, Iowa.	20	st.	st.	st.	st.	v.st.	v.st.
23	Marion silt loam; Unionville, Iowa.	none	st.	v.st.	v.st.	v.st.	v.st.	v.v.st.
24	Marion silt loam; Unionville, Iowa.	20	st.	v.st.	v.st.	v.st.	v.st.	v.v.st.
25	Carrington loam; Ames, Iowa.	none	st.	st.	st.	st.	med.	st.
26	Carrington loam; Ames, Iowa.	20	st.	st.	med.	st.	sl.	st.
27	Raw peat; Manistique, Mich.	none	c.n.b.r.	v.st.	v.v.st.	v.st.	v.v.st.	v.v.st.
28	Raw peat; Manistique, Mich.	200	c.n.b.r.	v.st.	st.	v.st.	st.	v.st.

*Nos. I and II solutions used on moist soil; no. II alone on dry soil.

†st., strong; med., medium; sl., slight; v.st., very strong; v. v.st., extremely strong; n.a., not acid; d.t.r., difficult to read; c.n.b.r., could not be read.

were weighed out in all cases, allowance being made for moisture. One-half as much peat by weight was used. The results are given in table 2.

Soiltex, the Truog test and the Comber potassium salicylate test gave the same results on the moist and dry soils. The Comber potassium thiocyanate test and Richorpoor gave the same results on some samples, but on others lighter colored solutions were secured with the moist soils. The Iowa test gave the opposite results. The moist soil often yielded much darker colored solutions than the dry soil treated with solution II alone. It was also found that when 2 cc. of solution I was added to a dry soil and shaken previous to the addition of the no. II solution, darker colors were secured than when 2 cc. of acetone was added in place of the no. I solution. However, when 2 cc. of

TABLE 3

Effect of drying soils on results secured with Richorpoor and Iowa tests

				RICHORPOOR TEST			IOWA TEST			
							Moist			
NUMBER	SOIL TYPE	H₂O CONTENT MOIST SOIL	pH VALUE	Moist soil	Air-dried at 25° C. for 3 hours	Dried at 85° C. for 3 hours	Solutions I and II	Ether and Solution II	Air-dried 3 hours Solution II	Dried at 85° for 3 hours, Solution II
		per cent								
1	Carrington loam............	26.0	5.2	sl.*	med.	st.	med.	med.	st.	st.
2	Carrington loam............	14.5	5.25	sl.	med.	st.	st.	st.	st.	st.
3	Carrington loam............	16.2	5.30	sl.	med.	st.	st.	st.	st.	st.
4	Carrington loam............	20.0	5.30	sl.	med.	st.	st.	st.	st.	st.
5	Carrington loam............	20.0	5.45	sl.	med.	st.	st.	med.+	st.	st.
6	Carrington sandy loam......	12.6	5.40	neut.	sl.	med.	med.	med.	med.	med.
7	Clinton silt loam...........	35.0	5.75	n.a.	sl.	med.	n.a.	n.a.	med.	med.

*sl., slight; st., strong; med., medium; n.a., not acid; neut., neutral.

ether containing no ammonium molybdate was added to a soil in place of solution I, equally dark colors were secured which would indicate that the addition of ether to the acetone solution containing potassium thiocyanate, results in a mixture which is capable of dissolving more iron from an acid soil than the acetone solution alone.

A further test was made on 7 field soils containing from 12.6 to 35 per cent of moisture. Each soil was divided into three parts; one portion was left moist, another was air-dried at 250°C. for 3 hours and the third was dried at 85°C. for three hours. The Truog test and the Soiltex gave the same results on all of the samples whether dry or moist. The Iowa test and Richorpoor were then tried. Two cubic centimeters of solution I and 8 cc. of solution II of the Iowa test were compared with 2 cc. of ether and 8 cc. of solution II on the moist soils. Only solution II was used on the dry soils. The results are given in table 3.

The Richorpoor test gave three different degrees of acidity on the soils used in table 3, depending upon the condition of the soil. There was practically no difference in the results secured with the Iowa test when solution I was used previous to solution II, or when ether was used before solution II. These results would indicate that in most cases phosphorus is not an inhibiting factor as suggested by Emerson (4). When the moisture content of a soil is below 20 per cent, solution II of the Iowa test gives practically the same results on moist soil as with dry soil, if an equivalent amount of soil is tested. Five grams of dry soil poured into a test tube occupies only about one-half as much space as 6 gm. of soil containing 20 per cent moisture. For this reason, an error may be made in field tests due to the fact that about the same volume of soil is used for a test whether it is wet or dry. This difficulty may be easily overcome by adding the test solution first and then the soil until a definite volume of suspension is secured.

It was found also that the fineness of the soil influences the tests measuring replaccable iron. Acid soils which are pulverized to pass a 60-mesh sieve give a darker color than the same soils ground to pass a 20-mesh sieve. This is due in part to the greater amount of surface exposed in case of the finely divided soils and also to the short period of agitation.

EFFECT OF VARIOUS ORGANIC SOLVENTS ON COLOR OF FERRIC THIOCYANATE
    AND AMOUNT OF IRON EXTRACTED FROM SOIL WITH VARIOUS SOLUTIONS
    CONTAINING 1 PER CENT OF POTASSIUM THIOCYANATE.

The color produced by ferric thiocyanate in solution is due, according to Prescott and Johnson (7), to the undissociated molecules. Natanson (6) found that the addition of ether to an acid solution containing a small amount of ferric thiocyanate caused a marked increase in color which appeared in the ether layer after the solutions were vigorously shaken. Marriott and Wolf (5) found that the color produced by ferric thiocyanate in an ether solution was not stable enough for quantitative analysis, and suggested the use of acetone which also increased the amount of color by decreasing the dissociation, produced colors which were stable when exposed to light and possessed another advantage of being miscible with water.

In this investigation, when 0.007 mgm. of iron, as ferric chloride, was added to 10 cc. of various organic solvents containing 1 per cent of potassium thiocyanate, it was found that different colors were produced similar to those secured when an acid soil is extracted. The colors produced by extracting an acid soil with various organic solvents containing 1 per cent of potassium thiocyanate are given in table 4.

When water was added to these various organic solutions, the color began to fade and soon disappeared except in the case of ethyl acetate which is only slightly soluble in water. It was also found that more iron was dissolved by some of the solutions than others, containing the same amounts of potassium

thiocyanate.   This was tested by shaking 5 gm. of soil and an equal volume of each of the various potassium thiocyanate solutions and centrifuging to secure a clear extract which was evaporated and then taken up with water containing a little hydrochloric acid.   The ethyl acetate solution replaced more iron than any of the others used.   The acetone solution was second in the amount of iron dissolved.   Methyl and ethyl alcohol solutions were about equal, extracting much less iron than the acetone solution.   An aqueous solution of potassium thiocyanate did not extract enough iron to give a color.

A neutral ethyl acetate solution containing 1 per cent of potassium thiocyanate will dissolve some iron from neutral and basic soils.   It is evident that such a solution is not as desirable as an acetone solution of potassium thiocyanate which settles just as rapidly and does not dissolve iron from neutral and

TABLE 4

A study of the colors produced by extracting a soil with different organic solvents containing 1 per cent of potassium thiocyanate

NUMBER	ORGANIC SOLVENT	KCNS	COLOR* COMPARISON	PLATE NUMBER
		per cent		
1	Acetone........	1	Scarlet red †	1
2	Acetone................................	5	Scarlet red +	1
3	Methyl alcohol.........................	1	Rhodanite pink—	38
4	95 per cent ethyl alcohol.................	1	Light Jasper red	13
5	50 per cent acetone, 50 per cent ethyl alcohol	1	Nopal red	13
6	50 per cent acetone, 50 per cent methyl alcohol	1	Jasper red	13
7	10 per cent acetone, 90 per cent ethyl alcohol..	1	Jasper red—	13
8	10 per cent acetone, 90 per cent methyl alcohol	1	Rhodanite pink	38
9	Richorpoor..............................		Nopal red—	13
10	90 per cent neutral ethyl acetate, 10 per cent ethyl alcohol.........................	1	Spectrum red	13

*Color Standards and Nomenclature by Ridgway (8).
†Colors selected with the assistance of A. M. O'Neal.

basic soils.   An acetone solution of potassium thiocyanate also possesses certain advantages over methyl or ethyl alcohol solutions because soil suspensions settle more rapidly in it, more iron is dissolved which gives a deeper color for comparison, and most important of all, it is less affected by moist soils. Also, Emerson[2] has found that potassium thiocyanate was more stable in an acetone solution than in a solution of 95 per cent ethyl alcohol, because of the lower amount of water present in the acetone.   Water decomposes potassium thiocyanate, liberating free sulfur.   The rate of decomposition is not seriously affected by light, but depends upon the amount of water present. For this reason old solutions of Potassium thiocyanate made up in solvents containing considerable amounts of water may give inaccurate results.

[2] Unpublished data.

CONCLUSIONS

Several qualitative tests for soil acidity were studied with 51 soils secured from Wisconsin, Missouri, Illinois and Iowa. All of these tests indicated, in a general way, differences between strongly acid, medium acid and slightly acid soils. Soiltex also distinguished between neutral and basic (alkaline) soils. The fact that this test requires very little equipment is a desirable feature. The chief difficulties encountered were with peat soils and heavy clay soils from which extracts could not always be secured clear enough for comparison with the Soiltex reaction chart.

The Truog test required more equipment than any of the others and also more time to make the test. This disadvantage is probably not so important when the accuracy of the results are considered. The same amount of each material is always measured for the test, which is not the case with the Comber potassium thiocyanate test and its two modifications, Richorpoor and the Iowa test, as they are being used at the present time by county agents and field men. More accurate results would be secured with these tests if calibrated tubes were used into which an accurate amount of liquid is measured and then soil added until a definite volume of suspension is obtained.

The Truog test and the Comber potassium salicylate test were the only methods which gave accurate results on very wet soils. Satisfactory results with Soiltex can be secured on soils which give low results with the potassium thiocyanate test because of the high moisture content. In the case of soils which contained less than 20 per cent of moisture, the Iowa test gave accurate results, while the Richorpoor test did not give satisfactory results except on dry soils.

Different colors are produced when ferric thiocyanate is formed in various organic solvents. These colors are much darker than the color produced when the same amount of a soluble ferric salt is added to an aqueous solution of potassium thiocyanate. This is probably due to the fact that organic solvents decrease the dissociation of the ferric thiocyanate molecules.

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THE COMPARATIVE EFFECTS OF ADDITIONS OF NITROGEN, PHOSPHORUS AND POTASSIUM ON THE NITROGEN ECONOMY OF A WOOSTER SILT LOAM SOIL[1]

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INTRODUCTION

Since nitrogen is one of the most essential plant constituents, is the most expensive to replace in the soil and furthermore is easily lost through leaching, it is obvious that methods of soil management which result in the conservation of the residual nitrogen in the soil and in the most efficient use of the applied nitrogen are of great importance to agriculture.

Such methods of soil management have received a great deal of attention from scientific investigators during the last half century and, although much valuable information has been obtained, nitrogen economy is still a most important problem.

MATERIAL AND OBJECT

The five-year-fertility rotation plots of the Ohio Agricultural Experiment Station are peculiarly adapted to a study of some of the factors which have a bearing on nitrogen economy. These plots on which experimental work was started in 1894 by former Director C. E. Thorne, are among the oldest and most carefully planned field plot tests in this country. The object in starting this work was to study the effects of additions of nitrogen, phosphorus and potassium fertilizers when applied alone and in combination, in different amounts and with different carriers, on the soil and on crop production. It is the object of this paper to discuss the apparent effect of these additions of nitrogen, phosphorus and potassium on the nitrogen economy of the soil.

HISTORICAL

Effect of fertilizer treatments on the conservation of soil nitrogen

It is generally conceded that aside from the removal of nitrogen from the soil in crops, the most serious loss is that occasioned by the leaching out of

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the nitrate nitrogen in the drainage water. Fertilizer applications have a tendency to check this loss. By stimulating crop production they cause a greater proportion of the nitrate nitrogen in the soil to be taken up in the increased crop, thus leaving a smaller amount to be leached out in the drainage water. A part of the nitrogen thus conserved by the larger crop is again returned to the soil in the increased crop residues.

This effect of fertilizer treatment is well demonstrated by the data reported by Russell (7) in comparing two plots, one of which received ammonium salts alone and the other, ammonium salts plus phosphorus and potassium. Although the latter plot produced 67 per cent more grain and over twice as much straw, there was an annual saving by this plot of 16.5 pounds of nitrogen through the more efficient assimilation of the nitrates produced in the soil.

This point is again emphasized in Dyer's (3) discussion of the results obtained in the continuous-culture wheat plots on Broadbalk Field at Rothamsted. Plot 5 in that work has received for 50 years a full supply of minerals without any nitrogen. As compared with the unmanured plot 3, it has yielded annually a crop amounting to 2 bushels of grain and 100 pounds of straw more than plot 3. Notwithstanding this increased removal in crops of about 5 pounds per acre per annum for 50 years, the surface soil of plot 5 contains about 108 pounds of nitrogen more than plot 3 and no diminution is indicated in the second and third depths. Dyer concluded: "This difference is clearly to be attributed to crop residue and the fact that plot 5 is now richer in nitrogen than plot 3 is due to storing up in stubble and root residue of a portion of the natural soil nitrogen, that without mineral manure to aid in its accumulation, would have been lost, as in the case of plot 3, in drainage."

Similar results were reported by Dyer (3) on a series of plots, all of which received the same amount of ammonium salts, but with different amounts of mineral fertilizers. The treatments were made in the years 1852–1893. The results show that as the amount of mineral fertilizer applications was increased, crop production was increased and the nitrogen content of the soil in 1893 was directly proportional to the amount of crop production. Dyer concluded: "The more completely by the supply of minerals the crops have been enabled to utilize the nitrogen supplies, the more have they accumulated in the soil; and conversely, the less that is utilized, the less is retained."

The influence of fertilizer treatment on the nitrogen balance as shown by cylinder and field experiments

The term "nitrogen balance" as used in this paper refers to the difference between the income and outgo of nitrogen in the soil. To determine the nitrogen balance of a soil at least four factors should be known.

  a. The nitrogen content of the soil at the beginning of the experiment.
  b. The amount of nitrogen added in fertilizers, etc.

c. The amount removed in the crops.

d. The amount of nitrogen in the soil at the end of the experiment.

A number of cylinder experiments have been conducted to study the nitrogen economy of different soils. One of the most extensive and carefully planned was reported by Lipman and Blair (4). Their data show the influence of phosphorus and potassium in conserving the nitrogen supply of the soil. A recalculation of their data shows that, in spite of the fact that the crops harvested from the cylinders given this treatment carried away an average of 85 pounds of nitrogen more than the untreated cylinders, the nitrogen balance showed a greater loss of soil nitrogen from the untreated cylinders amounting to 57 pounds. Cylinders receiving lime lost about half as much nitrogen as the unlimed, while those receiving a green manure crop in addition to lime lost about half as much as the limed cylinders.

Taking the average of the cylinders receiving each treatment, the order of the fertilizer treatments with respect to their efficiency in conserving the nitrogen supply of the soil was as follows: (1) P, K, 1N; (2) P, K; (3) Check: (4) P, K, 2N.

Lipman and Blair (5) also carried out a cylinder experiment to test the relative value of nitrogen in the forms of nitrate of soda, green manure crops and stable manure. In this experiment also the addition of the minerals, phosphorus and potassium had a conserving action on the nitrogen supply of the soil, although more nitrogen was removed in the crops on the plot receiving this treatment than on the check plot.

A cylinder test to compare the relative nitrogen economy of four Tennessee soil types was conducted by Mooers (6). He concluded from this test that: "There appears to be throughout the experiments a direct relationship between the size of the crop and the quantity of nitrogen conserved, so that, with other factors constant, the greater the crop, the greater will be the conservation."

A number of field experiments bearing on the subject of nitrogen economy have been conducted. Such an experiment covering a period of 50 years was reported by Dyer (3) in a study of the nitrogen economy of certain variously fertilized plots. The nitrogen balance drawn up for these plots shows that phosphorus and potash have had a considerable influence in conserving both the nitrogen of the soil and that applied in fertilizers.

A recalculation of the data reported by Blair and McLean (2) shows that the order of the fertilizer treatments with respect to nitrogen conservation in their experiment was: (1) P, K, N; (2) P, K; (3) P, N, (4) K, N.

Plan of fertilization

The general plan of fertilization which has been followed in the five-year-fertility rotation work at the Ohio Agricultural Experiment Station is given in table 1.

During the first five years the quantities of the elements applied to plots 21, 23 and 24 were the same as on plot 11, and the quantities of nitrogen and potassium on plot 30 were slightly smaller.

TABLE 1

Plan of fertilizing of 5-year rotation

Plots 0.1 acre; fertilizing materials in pounds per acre

PLOT NUMBER	ON CORN			ON OATS			ON WHEAT			
	Acid phosphate	Muriate of potash	Nitrate of soda	Acid phosphate	Muriate of potash	Nitrate of soda	Acid phosphate	Muriate of potash	Dried blood	Nitrate of soda
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
1										
2	80			80			160			
3		80			80			100		
4										
5			160			160			50	120
6	80		160	80		160	160		50	120
7										
8	80	80		80	80		160	100		
9		80	160		80	160		100	50	120
10										
11	80	80	160	80	80	160	160	100	50	120
12	80	80	240	80	80	240	160	100	50	200
13										
14	80	80	160				160	100	50	120
15							160	100	50	120
16										
17	160	80	80	160	80	80	160	100	25	60
18	Barnyard manure, 8 tons on corn and 8 tons on wheat									
19										
20	Barnyard manure, 4 tons, on corn and 4 tons on wheat									
21	Same elements as 17, but nitrogen in oilmeal									
22										
23	Same elements as 17, but nitrogen in dried blood									
24	Same elements as 17, but nitrogen in sulfate of ammonia									
25										
26	Same elements as 11, but phosphorus in bonemeal									
27	Same elements as 17, but nitrogen in nitrate of lime									
28										
29	Same elements as 11, but phosphorus in basic slag									
30	Same elements as 17, but nitrogen in tankage									

The block of $30\frac{1}{10}$ acre plots known as section D was selected for the study, since this section received lime on the west half only, and since it has the most uniform topography.

It was not until the beginning of the third complete rotation that lime was applied on section D. Caustic lime was applied at the rate of 1000 pounds per acre on the west halves of all the plots in the fall of 1903 previous to the

corn crop of 1904.   In 1909 ground limestone was applied at the rate of 1 ton and in 1914 at the rate of a little over 2½ tons and in 1919 at the rate of about 2 tons per acre.

Data

When the experiment was started in 1894 samples were taken from each plot. Some of these either have been used up in analytical work or were lost, only 17 of them remaining,   These remaining samples were reanalyzed at this time so that the analytical work on both sets of samples might be strictly comparable.   The results of the analyses, together with the number of the plot from which they were taken, are given in table 2.

TABLE 2

Nitrogen content of the soil—1894

PLOT	NITROGEN
	per cent
1	0.1040
3	0.0980
4	0.1000
6	0.1055
7	0.1045
8	0.1120
10	0.0980
11	0.1080
16	0.1115
18	0.1035
20	0.1000
22	0.0940
23	0.1145
24	0.1045
25	0.1130
26	0.1205
28	0.1005
Average..............................	0.1055

These samples previously had been analyzed and the data reported (1). Where the results obtained in 1921 differed from those previously reported, they were checked by another chemist.

The methods of sampling and preparation of samples were somewhat uncertain at that early date and since the nitrogen content of the soil as shown by the data varies quite widely from plot to plot, it has been thought advisable in calculating the loss of nitrogen to use the figure representing the average of all the plots.

A set of samples taken from these same plots in 1911 also was available. Some of these had been analyzed and the data reported (1).

As in the case of the 1894 samples, when the results of analysis in 1921 differed from those previously obtained, the determinations were checked by another chemist. The data are given in table 3.

Samples of soil were secured in the fall of 1921. The plots were then in young clover following the wheat crop. A 1-inch sampling tube was used, samples being taken to a depth of 7 inches. Forty borings were made on each

TABLE 3

Nitrogen content of soil 1911 and 1921

PLOT NUMBER	PER CENT OF NITROGEN				NITROGEN—POUNDS PER ACRE			
	Unlimed		Limed		Unlimed		Limed	
	1911	1921	1911	1921	1911	1921	1911	1921
1	0.0905	0.0782	0.0915	0.0813	1,810	1,564	1,830	1,626
2	0.0885	0.0781	0.0920	0.0810	1,770	1,562	1,840	1,620
3	0.0860	0.0746	0.0920	0.0746	1,720	1,492	1,840	1,492
4	0.0855	0.0746	0.0840	0.0746	1,710	1,492	1,680	1,528
5	0.0845	0.0752		0.0781	1,690	1,504		1,562
6		0.0797		0.0831		1,594		1,662
7	0.0810	0.0710	0.0895	0.0776	1,620	1,420	1,790	1,552
8	0.0870	0.0774	0.1030	0.0855	1,740	1,548	2,060	1,710
9		0.0740		0.0801		1,480		1,602
10	0.0640	0.0674	0.0785	0.0712	1,280	1,348	1,570	1,424
11	0.0880	0.0822	0.1010	0.0889	1,760	1,644	2,020	1,778
13	0.0995	0.0822	0 0975	0.0821	1,910	1,644	1,950	1,642
16	0.0915	0.0796	0.0840	0.0766	1,830	1,592	1,680	1,532
17	0.0965	0.0896	0.0980	0.0921	1,930	1,792	1,960	1,842
18	0.1170	0.1040	0.1160	0.1021	2,340	2,080	2,320	2,042
19	0.0930	0.0860	0.0825	0.0835	1,860	1,720	1,650	1,670
20	0.1030	0.0974	0.1010	0.0955	2,060	1,948	2,020	1,910
21	0.0945	0.0891	0.0965	0.0875	1,890	1,782	1,930	1,750
22	0.0890	0.0811	0.0775	0.0723	1,780	1,622	1,550	1,446
24	0.0920	0.0860	0.0970	0.0868	1,840	1,720	1,940	1,736
25	0.0890	0.0816	0.0990	0.0898	1,780	1,632	1,980	1,796
26	0.0855	0.0802	0.0890	0.0786	1,710	1,604	1,780	1,572
27	0.0930	0.0836	0.1000	0.0853	1,860	1,672	2,000	1,706
28	0.0795	0.0764	0.0845	0.0715	1,590	1,528	1,690	1,430
29	0.0885	0.0874	0.0960	0.0844	1,770	1,784	1,920	1,688
30	0.0910	0.0810	0.1050	0.0890	1,820	1,620	2,100	1,780
Average....	0.0897	0.0814	0.0937	0.0828	1,794	1,629	1,873	1,658

of the limed and unlimed plots. The samples were placed in trays as soon as they were brought in from the field, and dried in a chamber designed especially for this purpose. When thoroughly dried, the soil was ground and passed through a 0.5-mm. sieve. The samples were then analyzed for total nitrogen, according to a modification of the Gunning-Hibbard method. The results are given in table 3.

TABLE 4

Nitrogen added in fertilizer 1894–1921

PLOT	POUNDS PER ACRE	PLOT	POUNDS PER ACRE
1	0	17	266
2	0	18	768
3	0	19	0
4	0	20	384
5	456	21	266
6	456	22	0
7	0	23	266
8	0	24	266
9	456	25	0
10	0	26	456
11	456	28	0
13	0	29	456
16	0	30	266

TABLE 5

Total crop production, 1894–1921

PLOT	UNLIMED	LIMED
	pounds per acre	*pounds per acre*
1	46,729	66,328
2	62,589	86,017
3	41,454	65,329
4	36,983	60,350
5	45,981	70,040
6	76,970	96,467
7	38,601	59,807
8	73,425	99,251
9	53,961	79,992
10	39,972	63,624
11	88,343	121,320
13	44,714	69,534
16	41,375	65,713
17	91,641	125,003
18	100,407	128,180
19	47,836	74,834
20	78,711	101,949
21	90,043	112,693
22	42,693	62,421
23	79,709	108,204
24	73,776	113,553
25	47,071	66,494
26	83,209	102,872
28	34,003	55,828
29	83,215	102,703
30	78,091	103,497

Amount of nitrogen added in fertilizer

The amount of nitrogen added to the plots in fertilizer is given in table 4. These figures are not absolute, in that the nitrogen has not been determined by analysis before application in every case. Standard grades of fertilizers have been used, however, and in many cases the claims of the fertilizer companies have been checked by analysis in the laboratory.

Total crop production

The total crop production for each limed and unlimed plot is given in table 5.

DISCUSSION

It at once becomes evident that there has been a marked loss of nitrogen from the soil of these plots. The nitrogen supply of 2110 pounds per acre in 1894 diminished to an average of 1644 pounds in 1921, or a loss of about 22

TABLE 6

Comparative average annual losses of nitrogen and crop production of limed and unlimed plots expressed in pounds per acre

	1894–1911				1911–1921			
	Amount of nitrogen lost from soil		Total crop production		Amount of nitrogen lost from soil		Total crop production	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
Average of all plots............	17.5	13.1	2,308	2,763	15.0	19.5	1,893	3,388
Average of all checks..........	22.2	21.8	1,589	1,991	14.2	15.9	1,217	2,603
Average of all fertilized plots....	14.4	7.2	2,757	3,245	15.6	22.6	2,315	3,878

per cent. Figures showing the average annual losses of nitrogen and the average total crop production for the periods 1894–1911 and 1911–1921 are given in table 6.

It is interesting to note that in the period from 1911 to 1921, the tendency has been for the loss of nitrogen from the unlimed plots to be lessened, while the loss from the limed ends has apparently been accelerated.

Whether this increased loss of nitrogen from the limed plots is due to the lime stimulating the biological processes, resulting in the breakdown of the organic nitrogen into available nitrogenous compounds which are taken up by and carried away in the larger crops produced on these plots, is not known, since only a few of the crops have been analyzed. The data that are available however, tend to support this view. Also it will be noted that there is a decided increase in the crop production on the limed plots during the period 1911–1921, while on the other hand the tendency has been for the crop production to fall off slightly on the unlimed plots.

Conservation of soil nitrogen through increased yields

The data which bear on the effect of fertilizer treatments as conservers of the soil nitrogen through the more efficient utilization of the available nitrogen are summarized in table 7.

During the progress of the work here reported, a statistical study was made of the data on file, giving analyses of the crops grown on the different plots of the five-year-fertility rotation. The analyses were made on all the crops but for a few years only. After a careful study of these data an attempt was made to calculate the amount of nitrogen removed from each of the plots during the years 1894–1921. While the total amounts arrived at by this method are undoubtedly much too high, there is reason to believe that for comparison of

TABLE 7

Comparison of fertilized plots with regard to crop production and nitrogen conservation

Data expressed in pounds per acre

PLOT	TOTAL CROP PRODUCTION		NITROGEN LOST FROM SOIL		NITROGEN REMOVED IN CROPS (CALCULATED)	
	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
Average check	64,493	41,998	568	556	816	553
2	86,017	62,589	490	548	1,060	788
3	65,329	41,454	618	618	834	543
5	70,040	45,981	548	606	885	600
8	99,251	75,425	400	562	1,252	930
6	96,467	76,970	448	516	1,157	965
9	79,967	53,961	508	630	986	690
11	121,320	88,343	332	466	1,425	1,047
17	125,003	91,641	268	318	1,447	1,086
18	128,180	100,407	68	30	1,550	1,250
20	101,949	78,711	200	162	1,260	998

one plot with another, they come somewhat near the truth. The figures for the most important plots are given with the other data in table 7.

The averages of the total crop production of the limed and unlimed check plots show that the limed plots produced 36 per cent more than the unlimed plots, yet the limed plots lost only 2 per cent more nitrogen from the soil. Chemical analysis of the crops grown on the limed and unlimed ends of these check plots has shown very little difference in the percentage of nitrogen in the crops; the nitrogen content of the crops grown on the limed side is slightly higher, however.

Even if it is assumed that the amount of nitrogen removed in the crops from plots 2, 3 and 5 was the same for each of the plots, the order of nitrogen conservation is identical with the order of crop production, and this is in spite of the fact that plot 5 has received in fertilizer and lost 456 pounds of nitrogen in

addition to the loss of 548 pounds from the store of nitrogen in the soil, making a total loss of 1004 pounds.

Considering the plots which received fertilizer treatments containing two elements, plot 8 which receives phosphorus and potassium gave a greater crop production on the limed end than plots 6 and 9 which receive phosphorus and potassium, respectively, plus nitrogen.

In spite of the fact that they did not produce as large crops as plot 8, plots 6 and 9 lost more of their original supply of organic nitrogen and lost, in addition, the 456 pounds supplied to them in fertilizer.

In the same manner, plot 17, although raising larger crops and receiving only half as much nitrogen, has maintained the nitrogen supply of the soil at a higher level than plot 11. The application of 8 tons of manure on plot 18 has resulted

TABLE 8

Order of fertilizer treatments with respect to their relative efficiency in conserving nitrogen

ORDER OF TREATMENTS WITH RESPECT TO ABILITY TO CONSERVE THE SOIL NITROGEN		ORDER OF TREATMENTS WITH RESPECT TO ABILITY TO CONSERVE THE NITROGEN ADDED IN FERTILIZER AS WELL AS THE SOIL NITROGEN	
Plot	Fertilizer treatment	Plot	Fertilizer treatment
18	Manure, 8 tons	17	2 P, K, 1 N
20	Manure, 4 tons	8	P, K
17	2 P, K, 1 N	18	Manure, 8 tons
11	P, K, 2 N	2	P
8	P, K	20	Manure, 4 tons
6	P, N	11	1, P, K, 2 N
2	P	6	P, N
9	K, N	3	K
5	N	9	K, N
3	K	5	N

in an increased crop production as compared with 4 tons on plot 20, and has also better maintained the nitrogen supply of the soil.

Another striking comparison brought out in this table is that of the limed and unlimed ends of all the plots. Disregarding the fact that the calculated removal of nitrogen in the crops of the unlimed plots is only about 80 per cent of that of the limed plots, the data show that with the exception of the manured plots 18 and 20, and plot 3 receiving potash, the unlimed ends of these plots have lost from 50 to 130 pounds of nitrogen per acre more than the limed plots.

The relative efficiency of the different fertilizer treatments in conserving nitrogen is shown in table 8.

In figuring the relative efficiency in conserving both the original supply in the soil and that added in fertilizer, use was made of the calculations of the nitrogen removed in crops.

SUMMARY

1. Cropping a Wooster silt loam soil to a 5-year rotation of corn, oats, wheat, clover and timothy for 30 years has resulted in an average loss of 22 per cent of the original supply of soil nitrogen regardless of fertilizer treatment.

2. The limed ends of the plots have lost, on the average, nearly as much as the unlimed ends.

3. The tendency during the last 10 years has been for the limed plots to lose nitrogen faster than the unlimed plots.

4. Fertilizer treatments have resulted in a conservation of nitrogen directly proportional to the amount of increase in crop production due to the fertilizer treatment.

5. Liming has increased the amount of nitrogen conserved by most fertilizer treatments.

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THE INFLUENCE OF THE REMOVAL OF COLLOIDS ON SOME SOIL PROPERTIES

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In connection with some work at this station, on soil profiles, the effects of the colloidal particles in the soil were strikingly shown by the greater activity of certain horizons when compared to other horizons of similar mechanical composition. Studies have already been conducted upon the isolated colloids, from which it is assumed, one can ascertain the behavior of colloids in soils. But the properties of the colloidal mass when isolated and when disseminated throughout the soil may not be the same, owing to possible changes in the colloids during the process of removal. Since the soil particles of larger dimensions are probably less effected by the technique of colloidal removal than the colloids themselves, it was felt that a comparative study of a normal soil and the same soil without its colloids would be of interest.

To obtain suggestions with respect to this question two acid soils were chosen for a preliminary investigation. One of these soils was a surface sample of sandy loam with a rather high content of organic matter, while the other soil was of similar texture but almost lacking in organic material. Duplicate samples of each soil were suspended in water by shaking in a mechanical shaker for four hours, using a proportion of soil to water of 1 to 3. After washing down the sides of the containers, sedimentation was allowed to proceed for a period of forty-eight hours. At the expiration of this period the supernatant liquid was carefully siphoned off, and one sample of this liquid centrifuged for one hour. This was found sufficient to throw down the silt and clay, leaving the colloidal material in suspension. The solutions were poured off and the silt and clay returned to the mass of orignal soil. The liquid from the duplicate sample from each soil was placed in a Chamberland filter and the liquid passing through was discarded. The suspended material which coated the filter cone was removed and returned to the soil mass. This process was repeated six times. Thus the removal of the greater portion of the colloidal material from one sample and the retention of the same by the duplicate was accomplished, yet each were subjected to the same leaching, washing, and the same amount of shaking. Samples of the suspended material after centrifuging stood for 15 days without sedimentaton taking place. Thus, while an ultra microscope was not available, it was believed that only colloidal matter had been removed. After drying in the air to a point just below optimum moisture, the samples were screened, mixed thoroughly and stored in air tight containers.

Measurements of (a) the original hydrogen-ion concentration and the amount of lime water necessary to bring about neutralization, (b) the heat of wetting, and (c) the amount of water held free and unfree were made.

HYDROGEN-ION CONCENTRATION

Ten-gram samples of soil were placed in shaker bottles and 50 cc. of neutral distilled water added to one, another received 47.5 cc. of water and 2.5 cc. of 0.04 N calcium hydroxide solution, a third received 45 cc. of water with 5 cc. of calcium hydroxide solution, and so on, to that receiving 37.5 cc. of neutral distilled water and 12.5 cc. of limewater. These were shaken, mechanically, for four hours and allowed to stand twenty-four hours, after which pH readings were made electrometrically. The results are presented graphically in figures 1 and 2.
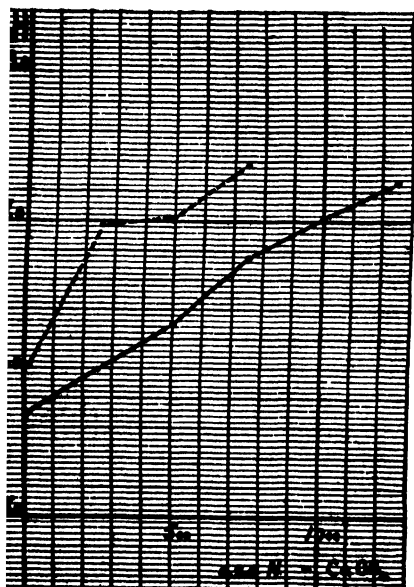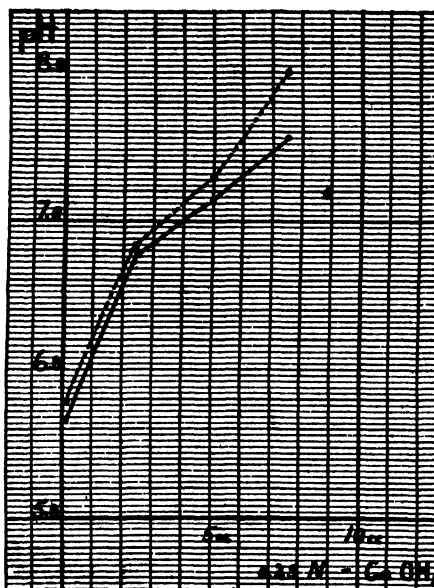
| FIG. 1 | FIG. 2 |

——————— Normal Soil
— — — — — Soil minus colloids

FIG. 1. TITRATION CURVES WITH LIMEWATER ON THE SOIL CONTAINING AN ABUNDANT SUPPLY OF ORGANIC MATTER

FIG. 2. TITRATION CURVES WITH LIMEWATER ON THE SOIL ALMOST FREE FROM ORGANIC MATTER

In both soils, the removal of colloids has caused the pH of the original soil to rise, showing less intense acidity in each case. The amount of limewater necessary to bring each soil to the neutral point was less in the case of the soils without colloids. There was less difference in this regard in the case of the sandy loam without organic matter, in which instance, there was but 0.3 cc. difference in the amounts of limewater necessary. The influence of organic colloids seems to be more intense, from the standpoint of buffering and in their

effect of the original pH of the soil. Bradfield (1) has shown that soil colloids are acid in nature, so that their removal should show somewhat definite changes in pH values and in the response to liming.

HEAT OF WETTING

Samples of about equal weight were measured out and dried in an oven at 105°C. for about thirty-six hours. After cooling in a desiccator the exact weight of soil was determined, and a thermometer graduated to tenths of one degree inserted into the container in such a way as to cover the bulb with soil. A calorimeter consisting of a thermos bottle of one quart capacity, fitted with a thermometer similar to the one above, and a stirring rod was used. Into it 100 cc. of pure distilled water was placed, and its temperature accurately read. When the temperature of the soil and water was the same, the soil was quickly emptied into the calorimeter and after stirring to wet the entire mass, the

TABLE 1

Heat evolved by 25 gm. of oven-dry soil on wetting

(Specific heat of soil = 0.2100)

SOIL	AVERAGE OF 2 TRIALS
	calories
Sandy loam with high organic content:	
Normal soil..	103.87
Without colloids..	94.15
Sandy loam with low organic content:	
Normal soil..	32.18
Without colloids..	28.26

temperature was read. Results have been reduced to the basis of the calories of heat evolved by 25 gm. of oven dry soil and are reported in table 1.

There is a lowering in the quantity of heat set free from soils when the colloidal influence has been removed, but the difference is not as striking as might at first be expected. The attraction of the surfaces for water is probably the same, whether such surfaces be on a large or a small particle of soil, but the total surface is lowered by the removal of the finer particles. There may also be a difference in activity of surfaces, in which case the colloidal surfaces would be the most active, and their removal should be factor of importance in the water relationships of soils as shown by these measurements. Further investigation seems necessary in this respect.

WATER RELATIONSHIPS

The dilatometer method in use in this laboratory was employed in this work and freezings made at temperatures of 1.5°C. and 4.0°C. below zero. According to Bouyoucos (2) the water which freezes at the first temperature is called

free water, while that which does not freeze at this point is called unfree. The latter type of moisture is again divided on the basis of the results from freezing at 4.0° below zero, into capillary adsorbed water and combined water. The capillary adsorbed form fails to freeze at the first temperature, but does solidify at 4.0° below. The remainder, which cannot be frozen at all is the combined form. Duplicate dilatometer determinations were made, which checked closely, and the results reported in table 2 are consequently averages, the total water added being considered as 100 per cent.

In the case of both soils the removal of colloidal material has resulted in a decrease in the amount of combined water held, and a corresponding increase in capillary adsorbed and free forms. It is not clear why the capillary adsorbed form should increase unless the removal of the colloidal coatings of certain larger particles has exposed fresh surfaces and fresh capillaries. In any event,

TABLE 2

Free and unfree water in soil

SOIL	FREE	UNFREE	
		Capillary absorbed	Combined
	per cent	*per cent*	*per cent*
Sandy loam with high organic content:			
Normal soil......	55.98	12.62	31.40
Without colloids...........................	58.02	15.88	26.10
Sandy loam with low organic content: .			
Normal soil	60.52	18.78	20.70
Without colloids...........................	62.86	21.18	15.96

these results show the influence of the finer portion of the soil on the combined forms of moisture. These bodies are evidently quite active in causing soil moisture to become inactive. The influence on the available moisture in soils seems worthy of special study.

SUMMARY

The removal of colloids from two soils brought about a rise in the pH value and a decrease in the amount of limewater necessary to bring about neutrality. The heat of wetting was decreased. The amount of water held in the combined form was decreased and the amounts of capillary adsorbed and free water were increased.

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THE INFLUENCE OF WATER ON SOIL GRANULATION

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INTRODUCTION

One of the most interesting physical phenomena in soils is the persistent tendency of soils to assume a granular structure when exposed to certain weather processes such as alternate drying and wetting. Natural soils of the fine-textured type, under normal conditions, nearly always possess this granular structure which is so desirable and important for the ultimate object—the successful growth of plants. In case the granular structure is destroyed by any means the soil soon recovers it upon being exposed to the above weather process. Even when a soil is worked to a plastic condition and becomes as dense and hard as a rock upon drying, it will crumble to a granular condition upon being subjected to alternate wetting and drying.

While there are several other factors or agents which tend to bring about a granular structure in soils—for example, freezing and thawing, addition of organic matter and lime, action of plant roots and animals, and tillage operations—the factor of alternate wetting and drying is probably the most important because it is universal and seems to be the most fundamental and most active.

However, there appears to be much vague and contradictory knowledge concerning the manner in which the process of alternate wetting and drying tends to cause granulation. It is the purpose of this paper, to point out what appears to be the true manner, and to emphasize the important rôle that the water plays in the process.

PREVALENT HYPOTHESIS

The formation of granular structure in soils as influenced by the process of alternate drying and wetting, is quite generally attributed to the pulling or contracting forces of the water films in the soil. It is claimed that as the moisture content of the soil is reduced by evaporation, the pulling power of the thinned water films is increased and they tend to bring or draw together the soil particles into granules, or floccules. This general idea is well expressed by Fippin (2), who says:

In studying these results one is led to inquire as to the force which brings this change or granulation. Clearly it is the water film. As the water content of the soil is reduced the sur-

face tension comes into play and draws the particles together. The smaller the particles the more easily they will be carried by this film. If the whole film around the wet soil mass contracted uniformly and as a unit the contraction would be manifested chiefly by withdrawal from the walls of the vessel and one dense mass would result. As a matter of fact the puddled soil is not homogeneous. There are inequalities or lines of weakness and these should determine the location of cracks. It also suggests that neither the continued wet condition nor the continued dry condition brings about any change in structure. The contraction of the water film is the primary force and it acts in conjunction with lines of weakness to bring about granulation. Anything which produced a line of weakness in the soil mass would determine the location of a crack.

Along the same subject Cameron (1) says:

The function of the film water in maintaining the soil structure is undoubtedly important . . . . The individual grains of soil are gathered into groups or floccules. While other causes may be more or less operative in particular cases, it seems very probable that the film water is primarily the agency holding together the grains in these floccules. The obvious explanation is that the film is exerting a holding power because of its surface tension. It follows, therefore, that anything which affects the surface tension of water should affect the structure of the soil, that is, the flocculation or granulation of the particles.

In further proof of the prevalence of the film hypothesis may be quoted Searle (3) who says:

The more general idea (which states facts rather than explains them) is that, as the water is removed, any which remains draws the clay particles together into a smaller and denser mass.

Inadequacy of present hypothesis

Upon critical examination, the actual facts not only fail to support the water film hypothesis as accounting for the granule structure in soils, but even contradict it. In the first place, it must be remembered that soil granulation signifies not only the combining of the single particles into compound particles or groups but also the breaking down or crumbling of dense masses of soil such as are found in compacted and puddled soils, subsoils, clods, etc., into loose and granular structure. If the water films tended to draw and hold the soil particles together, it logically follows that the soils would tend to remain in the dense condition and would not be reduced or crumble into the loose and granular structure.

In the second place, experimental evidence goes to show that the existing granular structure of soils under field conditions is due infinitely more to the breaking down or crumbling process than to the combining of single particles by the water films. As a matter of fact the part that water films play in the combining of single particles into compound particles is probably insignificant in comparison with the part that other factors play such as the flocculating agents, cementing materials, cohesive forces, etc.

In the third place, the power of water films to draw particles together or to cause the contraction of large masses of soil, as water is being withdrawn, seems to be greatly exaggerated. Considering the large friction and adhesive-

cohesive forces that the particles will have to overcome in moving at the low moisture content at which films operate, it does not seem reasonable and possible that water films have the pulling power to move and draw particles together. And some experiments which have been performed seem to support this contention. For instance, if single particles of clay are suspended in water upon glass, and care is taken to keep them apart during suspension, it is found that they do not come together as the water is reduced to films.

Probably one of the main reasons for attributing large pulling forces to the water films is the contraction of soils as they lose water. But examination shows that contraction and cracking will begin when the moisture content is still high and is probably not entirely reduced to films. For instance, some clay soils may have as high as 45 per cent of moisture when the contraction and cracking commences. Now it seems reasonable to assume that films cannot exert much pulling force until they are considerable reduced in thickness.

These latter facts, therefore, indicate that the contraction of soils is probably due to some force other than the pulling of the water film.

THE TRUE RÔLE OF WATER IN SOIL GRANULATION

From experimental studies that have been conducted as well as from logical reasoning it appears that water plays a leading rôle in the granular structure of soils but in a different way, and indeed just the opposite way, from what is commonly believed and expressed in the foregoing quotations. Water tends to draw apart or separate the particles from dense formation rather than draw them together. If the latter were true then there would be no loose and granular tilth of soils, but dense mass or clods. As has already been stated and as will be seen from plate 1, when clay soils are puddled and allowed to dry they become exceedingly dense and hard, and require tremendous pressure to break or crush them. If they are remoistened, however, and allowed to dry it is round that they are no longer as dense and hard as before, and require only a small pressure to break or crush them. If the process of drying and remoistening is repeated a few times, they may even crumble into granules or fine loose-textured pieces. In some soils, this crumbling may take place with only one wetting. Examination of the granules or small pieces shows that their single individual particles are held together in a rather loose condition and can be crushed easily by small pressure with the fingers.

This loosening of the particles of crumbling of the solid and dense masses of soil into granules or smaller pieces of loose structure, goes to prove that, on moistening, the water tends to loosen or separate the particles from too close contact and that on drying they do not come back to the original condition.

There appear to be at least two ways in which water is able to bring about a loosening of the solid mass and its final crumbling into granules or smaller pieces. These are (a) the swelling of the soil colloids and (b) the diminution of the attractive and cohesive forces of the soil particles by the intervening water.

As is generally known, soil colloids, and especially certain types, tend to expand or swell upon absorbing or being wet with water. When the dry dense solid masses of colloidal soils as described above, absorb water, they expand or swell, and their particles are loosened and pushed further apart, sometimes beyond molecular and attractive distances. When these masses of soil dry, the water films are not powerful enough to pull the particles together into as compact or dense condition as they were originally, but allow them to remain in the loose condition into which they were brought by the swelling. Upon further wetting and drying, the soil particles come further apart and they may finally crumble into granules or small pieces.

The loosening, pulling apart and shattering effect of the swelling of the colloids on the particles of the dry dense mass of soils is analogous to that of the freezing of water. The expansion that the water produces upon freezing shatters and pulls apart the soil particles and upon drying, the mass may crumble into granular structure.

The swelling of the colloids tends to facilitate the formation of granular structure in still another way, that is, by the unequal expansion that soil may undergo during the absorption of water. If the soil is moistened unequally, and unequal expansion takes place, there will be stresses set up which will tend to crack or shatter the soil mass.

The second way in which water is able to bring about a loosening of the solid mass and facilitate the development of crumb or granular structure, is by saturating the soil with an excess of water. It can be demonstrated easily that when a solid mass of soil is placed in an excess of water it immediately begins to slake or disintegrate into small floccules as shown in plate 1, figure 3. The process is really a mechanical dissolution somewhat similar to a chemical dissolution, but differing in degree. It is brought about by the attraction of the particles for water, and the film of water intervening or surrounding the particles destroying their force of cohesion or attraction for each other. When the mass is allowed to dry again the particles are no longer as close together as they were before and can easily be crushed. If the particles do not exist in an extremely fine state, and if too much cementing material is not present, after the soil mass is dried it may be left in a crumb structure or in a condition in which it can readily be reduced to crumb structure.

It must be emphasized that water is able to bring about the foregoing physical-structure in soils under conditions in which not much pressure is applied to press and interlock the soil particles together and thus destroy the loosening and crumbling effect of water. From this point of view it would seem that when a clay soil under field conditions has been puddled it would be better to plough it in order that the particles may be free of side pressure and have greater freedom to crumble. But even in unploughed condition, puddled clays tend to assume the granular or crumb structure by the process of wetting and drying.

The question now may be raised to the effect that if it is not the film of water that pulls the soil mass together as water is being withdrawn, what is it? The answer seems to be that it is the pulling forces of cohesion of the soil particles. The soil particles, of course, possess cohesive force, which is developed by the water, the degree of development depending to a great extent upon the colloidal content present. As the excess of water is withdrawn the colloids which had swollen, shrink and the cohesiveness, together with the interlocking of the soil particles, keeps the whole mass intact, and the mass shrinks or contracts as a whole. However, if there is too much friction for the whole mass to contract uniformly, it will crack and separate at the weakest points of contact, or at the most convenient point, or where the greatest pressure is brought to bear. The finer the particles and the closer they are together the greater will be the cohesive force and the denser will be the condition in which the mass will dry. For instance when a plastic clay is moulded into a ball or suspended into an excess of water and then allowed to dry, in either case the dry masss will be as hard as a rock. This hardness is due to the close packing and interlocking of the particles which are thus brought in closer range of molecular attraction and consequently of cohesive force, and also due to the cementing of the colloidal gels and certain inorganic salts. But as previously stated, when these dry and highly dense soils are moistened their particles are pushed apart, their range of molecular attraction and cohesive force is thereby decreased, and consequently the soils do not become as dense and hard when dried again.

No attempt has been made to discuss all the details that are involved in the process of granulation of soils as influenced by drying and wetting. It is purposed simply to show that water tends to granulate soils by its expanding forces rather than by its contracting forces.

SUMMARY

This paper presents a critique upon the rôle of water films on soil granulation. The general idea that the granule formation of soils is due to the pulling forces of the water films as it becomes thinned, appears to be incorrect. If it were correct, then the soil would tend to contract as a mass and into a dense structure condition, and there would be no granular structure. Soil granulation signifies not only the flocking together of the single particles into larger or compound particles, but also the breaking down or crumbling of dense masses of soil such as are found in dry puddled soils and clods, into the loose and crumb structure.

On the contrary, water brings about the formation of granular structure not by pulling the soil particles together but rather by pushing them apart, and thus giving rise to the crumbling of dense masses or clods into the loose and granular structure.

Water is able to accomplish this in two ways: (a) by the swelling of the colloids and (b) by diminishing the cohesive force of the particles as it (the water), comes between them and pushes them farther apart.

The forces of contraction are not due to the water films but to the cohesive force of the soil itself. Water, therefore, plays a very important part in the granulation of soils, but in just the opposite way from what is· commonly believed.

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PLATE 1

ILLUSRATIONS SHOWING THE TENDENCY OF WATER TO CAUSE DENSE AND HARD MASSES OF SOIL TO CRUMBLE INTO GRANULAR STRUCTURE

Fig. 1. The ball to the extreme left is as hard as rock; upon being moistened it cracks and begins to crumble as shown in the balls to the right.

Fig. 2. Block to the left is as hard as rock; upon being moistened it cracks and begins to crumble as shown in the next block of soil.

Fig. 3. Ball at the center is as hard as rock; upon being placed in excess of water it slakes into fine granules. When these granules dry, they are in a loose condition.
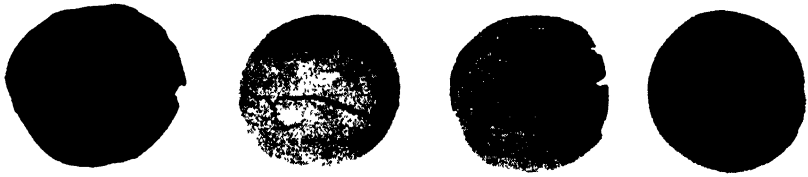
FIG. 1

FIG. 2
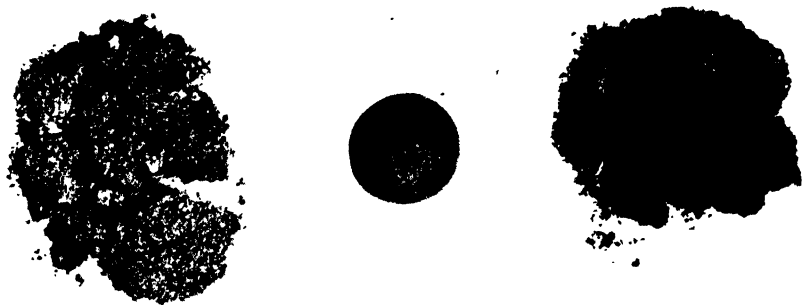
FIG. 3

SOME EFFECTS OF SULFUR ON CROPS AND SOILS[1]

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Considerable attention has been given recently to the use of sulfur as a fertilizer and its effect on the soil. In the experiments here reported the author tested the influence of sulfur on the germination and early growth of clover and alfalfa, and its effect on the acidity and solubility of the soils used. Also, the effect of leaching on the acidity produced by the sulfur treatment was investigated.

The experiments were conducted on a Coloma medium sand and a Miami silt loam. The sulfur to be used was washed with distilled water until it gave no freezing-point depression, and then was mixed with the Coloma sand at the rates of 0, 500, 1000, 1500, 2000, and 3000 pounds per acre, and with the Miami silt loam at the rates of 0, 1500, 2000 and 3000 pounds per acre. The former soil was made up to 10 per cent water content and the silt loam to 16 per cent. They were then stored in the dark, the moisture content being kept uniform during the course of the experiment by frequent weighing and the addition of water. At 10-day intervals, duplicate pots were filled with the soil, and planted to June clover and alfalfa. The stored samples were thoroughly mixed and aerated. The number of seedlings appearing above ground in these pots was taken to represent the germination except where no growth occurred, in which case the seeds were found in the soil and the percentage of germination determined. Germination was considered complete in 10-days, and the potted soils were air-dried and stored.

The total soluble salt content of the soils was measured by the freezing-point depression method as developed by Bouyoucos and McCool (1, 2). The acidity of the soils as expressed by pH values, was measured by electro-chemical means.

The results given are the averages of the duplicate pots. The acidity and freezing-point results are those of the soils after potting, so they really were incubated 10 days longer than the table would indicate. ·

From these results it appears that the sulfur had little effect on the germination and early growth of the plants, except where the large applications incubated for several weeks, in which cases the growth above ground was decreased. Attention may be called to the fact that in the case of the 3000-pound 60-day

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sand pots, 74 per cent of the alfalfa germinated, even though none of this came
through the soil; with the 3000-pound 30-day pots the germination was 33

TABLE 1

Germination of alfalfa and clover in Coloma sand incubated for periods as indicated

SULFUR APPLIED	0 DAYS		10 DAYS		120 DAYS		30 DAYS		60 DAYS	
	C	A	C	A	C	A	C	A	C	A
None..............................	94	62	84	51	89	59	91	68	88	65
500 pounds........................			89	55	82	56	84	64	91	62
1,000 pounds.......................	89	62	93	58	86	55	88	65	90	62
1,500 pounds.......................	90	67	91	51	89	64	89	59	78	42
2,000 pounds.......................	89	55	97	54	90	59	86	57	48	51
3,000 pounds.......................	88	57	90	60	94	49	5*	7*	0†	0†

A—Alfalfa.
C—Clover.
* {A, 33 per cent germinated but did not appear through soil.
  {C, 61 per cent germinated but did not appear through soil.

† {A, 74 per cent germinated but did not appear through soil.
  {C, 52 per cent germinated but did not appear through soil.

TABLE 2

pH values of sand incubated for periods as indicated

SULFUR APPLIED	0 DAYS	10 DAYS	20 DAYS	30 DAYS	60 DAYS
	pH	pH	pH	pH	pH
None............................	7.95	8.2	8.15	8.2	8.05
500 pounds......................	7.75	7.5	7.6	7.5	7.5
1,000 pounds....................	7.65	7.35	6.75	6.7	6.3
1,500 pounds....................	7.7	7.2	5.6	5.0	4.3
2,000 pounds....................	7.65	7.2	4.5	4.4	3.9
3,000 pounds....................	7.6	6.7	4.4	4.1	3.65

TABLE 3

Freezing-point depression of Coloma sand plus 30 per cent water

SULFUR APPLIED	0 DAYS	10 DAYS	20 DAYS	30 DAYS	60 DAYS
	°C.	°C.	°C.	°C.	°C.
None............................	0.007	0.016	0.017	0.015	0.017
500 pounds......................	0.011	0.028	0.042	0.043	0.042
1,000 pounds....................	0.034	0.037	0.043	0.043	0.047
1,500 pounds....................	0.041	0.045	0.047	0.051	0.070
2,000 pounds....................	0.041	0.043	0.058	0.060	0.080
3,000 pounds....................	0.045	0.051	0.060	0.073	0.112

per cent and the growth 7 per cent. This indicates that alfalfa seed will
germinate when the intensity of the acidity is too great for growth.

The acidity of the soils and the amount of soluble material increased with the amount of sulfur applied and the length of the incubation period. There appears to be a correlation between the pH values and the amount of soluble material present, and this is more apparent in the sand cultures. The increase in soluble salts in these soil is undoubtedly due, in a large part, to the biological oxidation of sulfur.

After reaching a certain hydrogen-ion concentration, a very slight change in acidity has a decided effect on the stand. This is shown in the sand where

TABLE 4

Germination and growth on Miami silt loam

SULFUR APPLIED	0 DAYS		10 DAYS		20 DAYS		30 DAYS	
	C	A	C	A	C	A	C	A
None....................	63	59	86	72	89	64	80	69
1,500 pounds.........................	89	62	90	64	93	60	73	63
2,000 pounds.........................	92	68	83	59	91	61	24	10
3,000 pounds.........................	86	64	74	54	70	52	2	0

TABLE 5

pH values of Miami silt loam

SULPHUR APPLIED	0 DAYS	10 DAYS	20 DAYS	30 DAYS
	pH	pH	pH	pH
None.......................	4.9	5.05	4.97	5.05
1,500 pounds...........................	4.85	4.35	3.95	3.62
2,000 pounds...........................	4.75	4.1	3.75	3.4
3,000 pounds...........................	4.75	3.5	3.4	3.16

TABLE 6

Freezing-point depressions of silt loam plus 35 per cent water

SULFUR APPLIED	0 DAYS	10 DAYS	20 DAYS	30 DAYS
	°C.	°C.	°C.	°C.
None.......................	0.011	0.019	0.017	0.021
1,500 pounds.........................	0.0215	0.042	0.0495	0.054
2,000 pounds.........................	0.023	0.051	0.076	0.085
3,000 pounds.........................	0.024	0.059	0.1045	0.1165

a fair growth occurred at pH 4.3, but practically none at pH 4.1, and in the silt loam where similar results were obtained at pH 3.5 and pH 3.4.

From the fact that growth practically ceased in the sand at pH 4.1 while in the silt loam the plants grew well at pH 3.5, it is apparent that the acidity at which a plant will grow is a property of the soil and not entirely of the plant itself, and will vary with the soil used. And it appears also that this is due to some effect on the growth of the seedling and not on germination. The hydro-

gen ion concentration produced in a soil by a certain treatment also is controlled by the soil itself, and results on different soils will not be strictly comparable.

In the sand cultures there was better growth in the 2000-pound—60-day pots, than in the 3000-pound—30-day pots although the former had the greatest content of soluble salts. Similar results may be found in the silt loam cultures. This fact would seem to indicate that the death point of the plants was not due to too great a concentration of the soil solution.

Samples of the untreated and treated sand cultures were placed in glass cylinders and leached by percolation with 5 liters of water. Samples of the leachings were taken after the first 250 cc. had passed through, and also the last 250 cc. of percolate was collected in each case. These leachings were analysed for Ca and SO₄ and the pH value was found. The hydrogen-ion concentration of soil samples taken after 4½ liters had passed through, also was found and compared with the same for the unleached soils.

These figures show that although the sulfate was practically all removed by leaching, the acidity produced by sulfur oxidation was not. On the contrary

TABLE 7

Results of leaching treated and untreated soils

	BaSO₄ IN 50 CC.	CaO IN 50 CC.	pH
Treated unleached soil	gm.	gm.	5.5
Treated leached soil			5.3
First leachings	0.0320	0.0085	5.6
Last leachings	Trace	Trace	4.4
Untreated unleached soil			7.5
Untreated leached soil			6.9
First leachings	0.0004	0.0010	7.5
Last leachings	None	Trace	5.6

leaching made the treated soil slightly more acid. Apparently the sulfuric acid reacted with the soil bases as fast as it was formed, and the increased soil acidity was due to insoluble acids or acid salts. The alkaline soil was made more acid by leaching, and the last leachings from this soil were strongly acid.

Practically all of the soluble calcium and sulfate sulfur were washed from the soil. The untreated soil contained essentially no sulfates. Although the untreated soil was alkaline and showed the presence of excess carbonate when treated with acid, the first leachings from the treated soil contained more calcium than those from the untreated. This shows that the treatment made the calcium more soluble. There was some evidence that the treatment flocculated the colloids present, inasmuch as the water percolated faster in the treated soil.

Lime-requirement determinations were made on some of the treated soils by an electrometric titration method developed by Spurway (3). The results show that although there may be some correlation between pH value and total

lime required to bring one soil to neutrality under different conditions, yet there is no correlation between these properties in different types of soil.

Some sulfur-treated plots on Plainfield loamy sand were planted to mammoth clover, and the acidity of soil samples taken at intervals during the summer was determined. The decrease in stand of clover and the increase in acidity varied directly with the amount of sulfur applied. On one of the plots, the pH value of which was 3.1 some clover was found growing four months after treatment.

<div align="center">ACKNOWLEDGMENT</div>

The author wishes to express his gratitude to Dr. M. M. McCool for outlining the methods of procedure and his many helpful suggestions during the progress of the work, and to Prof. C. H. Spurway for his assistance in interpreting the chemical determinations.

<div align="center">REFERENCES</div>

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A STUDY OF SEVERAL ORGANIC SOIL PROFILES[1]

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It is rather difficult to correlate results obtained by different investigators on the nutritional, ecological and other phases in which soils are employed as the media for plant growth because of a lack of satisfactory and standardized methods of measuring the physico-chemical properties of soils. For example, the profiles of the mineral soils of northern Michigan are composed of five distinct horizons, whereas those of the southern portion of the state have usually five distinct horizons differing markedly from soils of similar texture in the north (4). Differences in the amount and nature of the materials that go to make up the organic soil profiles have been observed (2). As Dr. C. F. Marbut has brought out (3), it is desirable to study soils as such, and much greater attention should be given to the various soil horizons. The indications are that the plant is influenced not only by the surface few inches of soil but by the properties of the horizons of the entire soil profile. Thus it seems that the ecologist would find it profitable to consider more carefully the various soil horizons while carrying on field investigations.

Although reports of physical investigations on mineral soils are legion, this is not the case with respect to organic soils. In this field we find much less information, yet it is probable that the physico-chemical relationships of these soils are almost as far-reaching in their effect on plant growth, the methods of fertilizing and other phases of their management, as they are with mineral soils.

It has been found mainly through the use of mineral soils that water in soils varies tremendously with respect to the temperature relationships (1). Some of it may freeze readily when the temperature is slightly below O°C., some may not freeze at this temperature but will solidify at or near − 2°C. and some may freeze at –4°C., while some may not solidify even at much lower temperatures. The water of soils has been classified on the basis of such properties. From the physiological aspect such relationships of the soil and moisture doubtless are of tremendous importance.

It is well recognized that dry soils when moistened give off heat and the number of calories of heat evolved varies considerably with different soils. Apparently the colloidal content and the state of the colloidal material has a great effect upon this phenomenon.

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It has long been known that wet peat shrinks markedly upon drying and this property is important from both the agricultural and the industrial standpoint. When organic deposits are drained it is possible that the degree of such shrinkage has an important bearing upon this practice.

It has occurred to us that these phenomena may be utilized in studying the physical properties of organic soils and perhaps assisting in their classification.

EXPERIMENTAL RESULTS

Dilatometer studies

It is possible, we found, during the progress of our investigations, that the water content of the soil used in dilatometer studies regulates somewhat the results obtained. Accordingly, dry materials were sampled in triplicate and treated with different amounts of water, well mixed, and allowed to stand in the moist condition two days before making the determinations.

Several samples were taken from the field and used in the moist condition. That is, they were not permitted to become air-dry before studies were made. One portion of each sample was placed in a closed container where it remained unchanged so far as moisture content was concerned, another portion was allowed to lose some moisture by evaporation and a third portion was permitted to lose still more.

It was considered important also to determine whether or not the air-drying of samples of organic soils results in a measurable change in the results obtained from dilatometer studies. For this purpose samples were brought from the fields, thoroughly mixed while wet, separated into two portions and their weights recorded. One portion was permitted to lose moisture by evaporation until it became air-dry, and then was made up again to the original weight with water before the studies were undertaken. According to the results presented in table 1 the amount of water that fails to freeze in the materials used is practically the same where the total water content is about the same, and air-drying does not affect the results obtained. Additional results are presented in conjunction with the heat of wetting studies.

A brief description of these materials and also of the materials mentioned in tables 3 and 4, is given in table 5.

Heat of wetting

It was brought out early that there is an appreciable difference in the time required for different materials to reach equilibrium when moistened (or to cease to generate heat upon becoming wet). It was apparent that if some samples were worked up at the proper moisture content and left in a porous condition they took up water readily, whereas if collected while quite wet and permitted to dry without being broken up they became very hard and relatively impervious, and even when crushed to very small particles took it up very slowly as indicated by the rate at which they generate heat.

TABLE 1

Unfree water held at different water contents

SAMPLE AND TREATMENT	WATER CONTENT	WATER HELD UNFREE PER 10 GM. OF OVEN-DRY MUCK
	per cent	*cc.*
Bope, 1st foot, air-dried..............................	101.06	4.94
Bope, 1st foot, air-dried..............................	123.98	4.99
Bope, 1st foot, air-dried..............................	152.85	5.13
Bope, 2nd foot, air-dried.............................	113.41	5.84
Bope, 2nd foot, air-dried.............................	169.60	6.49
Bope, 2nd foot, air-dried.............................	203.63	7.05
Town Line, surface, air-dried.........................	125.27	5.54
Town Line, surface, air-dried.........................	184.55	6.11
Town Line, surface, air-dried.........................	188.80	6.00
Farm Lane, surface, air-dried.........................	125.96	4.83
Farm Lane, surface, air-dried.........................	183.57	5.49
Farm Lane, surface, air-dried.........................	201.37	5.48
Town Line, surface, kept moist........................	121.58	5.63
Town Line, surface, kept moist........................	166.38	6.04
Town Line, surface, kept moist........................	191.45	6.27
Town Line, subsoil, kept moist........................	232.84	7.87
Town Line, subsoil, kept moist........................	346.15	8.36
Town Line, subsoil, kept moist........................	409.54	8.88
Farm Lane, surface, kept moist........................	128.86	5.57
Farm Lane, surface, kept moist........................	159.75	5.90
Farm Lane, surface, kept moist........................	179.93	6.22
Farm Lane, subsoil, kept moist........................	223.62	7.85
Farm Lane, subsoil, kept moist........................	335.58	8.39
Farm Lane, subsoil, kept moist........................	369.32	8.63
Town Line surface, dried and rewet....................	153.50	5.76
Town Line surface, kept wet...........................	153.19	5.92
Town Line subsoil, dried and rewet....................	297.84	8.04
Town Line subsoil, kept wet...........................	301.99	8.13
Farm Lane surface, dried and rewet....................	185.45	5.74
Farm Lane surface, kept wet...........................	152.35	5.48
Farm Lane subsoil, dried and rewet....................	302.65	8.41
Farm Lane subsoil, kept wet...........................	294.04	8.28

It was therefore thought advisable to determine the effect of the physical condition of the materials on the rate at which heat is generated. Some of the less pervious materials, or those that become very hard upon drying, taken from the third and fourth foot of a deposit, were used for these investigations. They were ground to different degrees of fineness and the heat of wetting determined.

Two samples mentioned above were used for this work and the operation was repeated twice with a slight change in the method. (A) In the first case the material was crushed to pass through a 3-mm. sieve. It was then divided in two equal parts, one being used to determine the heat of wetting without further change, while the other was quite finely ground without crushing the particles too much before using. (B) In the second case the material was crushed to pass a 3-mm. sieve, then it was sifted through a 2-mm. sieve and that which passed through was rejected, nothing being used except the lumps ranging in size from 2 to 3 mm. This material was divided into two equal

TABLE 2

Effect of physical condition on the heat of wetting

TREATMENT	DEPTH OF SAMPLE			
	Third foot		Fourth foot	
	Not ground	Ground	Not ground	Ground
Method A:				
Time (minutes)........................	42	8	46	8
Heat of wetting (calories)................	760.50	784.40	711.08	728.50
Method B:				
Time (minutes)........................	55	11	75	15
Heat of wetting (calories)................	738.90	760.00	675.00	695.00

parts, one of which was ground before being used. The results of this work are given in table 2.

The striking thing about these results is the great difference in the time required for materials of different fineness to generate the total heat upon being placed in water. It was observed that in case of the ground samples the most of the heat was produced in the first minute and the amount produced in each succeeding minute was less until the maximum was reached in 8 to 12 minutes. This indicates that the very fine material took up moisture readily and the small amount of slightly coarser material took up moisture more slowly. In the case of the unground soil, which ranged in size of lumps from very find up to 3 mm., the per cent of total heat produced in the first minute was much less, and for the material ranging from 2 to 3 mm. it was still smaller.

The heat of wetting of samples taken at different depths from several deposits also was determined. Thin slabs were cut from each and thoroughly mixed, while still moist, before using. The time required for those taken from several

TABLE 3

Loss on ignition, heat of wetting per 25 gm. of soil, and time required for soils to reach maximum temperature in heat of wetting

SAMPLE	LOSS ON IGNITION	HEAT OF WETTING PER 25 GM. OF MATERIAL	TIME REQUIRED TO REACH EQUILIBRIUM
	per cent	*calories*	*minutes*
Bope:			
1st foot.................................	65.8	766.6	8
2nd foot................................	83.1	787.5	12
3rd foot................................	85.7	700.8	13
4th foot................................	57.9	569.7	6
5th foot................................	47.2	506.5	6
6th foot................................	17.0	185.2	5
De Camp:			
1st foot.................................	81.0	954.5	5
2nd foot................................	85.3	933.9	7
3rd foot................................	87.3	900.6	3
4th foot................................	87.5	904.1	11
5th foot................................	85.6	83£.1	7
Homer:			
1st foot................................	84.0	901.3	8
2nd foot................................	89.3	847.7	12
3rd foot................................	76.9	708.3	15
4th foot................................	80.5	744.6	13
Thorp:			
1st foot.................................	84.8	846.4	8
2nd foot................................	86.9	884.0	5
3rd foot................................	89.6	815.5	4
4th foot................................	89.2	716.9	8
Hudsonville:			
1st foot................................	80.5	916.0	5
2nd foot................................	85.8	853.0	8
3rd foot................................	83.8	821.0	11
Kingery:			
0–5 inches............................	72.7	692.0	14
5–8 inches............................	85.2	636.0	12
8–16 inches............................	86.2	628.0	7
16–24 inches............	84.5	631.0	12
24–32 inches............................	78.5	635.0	9
Ingham County[1]:			
0–6 inches............................	78.3	457.7	
6–24 inches............................	72.4	456.6	
24–40 inches............................	82.3	341.0	

TABLE 3—*Continued*

SAMPLE	LOSS ON IGNITION	HEAT OF WETTING PER 25 GM. OF MATERIAL	TIME REQUIRED TO REACH EQUILIBRIUM
	per cent	*calories*	*minutes*
Ingham County[a]:			
0–15 inches.............................	81.2	722.0	
15–36 inches.............................	85.8 [a]	751.0	
Posen:			
0–4 inches.............................	80.1	769.7	
4–24 inches.............................	83.5	778.4	
24–36 inches.............................	88.3	788.8	
36–48 inches.............................	66.1	564.0	

TABLE 4

Unfree water, heat of wetting, and loss on ignition of surface materials

SAMPLE NUMBER	UNFREE WATER	HEAT OF WETTING PER 25 GM. OF MATERIAL	LOSS ON IGNITION	RATIO OF HEAT OF WETTING TO UNFREE WATER
	per cent	*calories*	*per cent*	
3	41.2	397.32	89.7	9.6
1	46.2	477.53	92.6	10.3
2	49.2	463.77	90.4	9.4
20	49.3	486.67	56.9	9.8
12	52.4	466.97	85.8	8.9
17	55.2	596.86	71.8	10.8
13	56.0	552.95	72.7	9.8
16	60.0	529.72	75.4	8.8
7	61.4	559.22	74.8	9.1
5	61.5	579.28	75.6	9.4
18	61.5	564.92	76.9	9.1
11	62.3	664.44	76.3	10.6
19	63.5	697.48	82.2	10.9
4	64.2	670.46	79.0	10.4
6	64.6	647.99	76.2	10.0
8	66.5	646.07	79.0	9.7
14	66.5	693.20	83.5	10.4
9	69.5	666.52	80.7	9.5
10	70.9	714.32	78.8	10.0
15	70.9	708.42	84.2	9.9

* In making these determinations 5 gm. of air-dry soil was moistened with 5 cc. of H_2O.

deposits to reach the maximum temperature, as well as the heat of wetting and the loss on ignition, is given in table 3. It seems that the best method of preparing the samples is to work them up with the hands when at the proper moisture condition, so that they will dry out to be granular and porous. Even with this treatment some of them are more or less resistant to wetting as the data in table 4 show.

TABLE 5

A brief description of materials mentioned in tables 1, 3 and 4

SAMPLE NUMBER OR NAME	COLOR	TEXTURE	VEGETATION
1	Brown	Coarse	Huckleberry
2	Brown	Coarse	Huckleberry
3	Brown	Coarse	Huckleberry
4	Dark brown	Finely divided	Tamarack
5	Dark brown	Finely divided	Tamarack
6	Dark brown	Finely divided	Cat tail
7	Brown	Finely divided	Huckleberry
8	Black	Finely divided	Tamarack
9	Black	Finely divided	Tamarack
10	Dark brown		
11	Dark brown		
12	Brown	Coarse	Huckleberry
13	Black	Finely divided	Black ash and elm
14	Dark brown	Medium fine	
15	Dark brown	Coarse	
16	Black	Finely divided	
17	Black	Finely divided	
18	Dark brown	Finely divided	
19	Black	Finely divided	
Town Line:			
Surface.....................	Black	Finely divided	
Subsoil.....................	Black	Finely divided	
Farm Lane:			
Surface.....................	Black	Finely divided	
Subsoil.....................	Dark brown	Slightly fibrous	
Bope:			
1st foot....................	Dark brown	Finely divided	
2nd foot...................	Dark brown	More woody	
3rd foot....................	Dark brown	Woody	
4th foot....................	Dark brown	Woody	
5th foot....................	Gray tinge	Sandy	
6th foot....................	Gray	Quite sandy	
DeCamps:			
1st foot....................	Brown	Coarse	
2nd foot...................	Brown	Woody	
3rd foot....................	Brown	Woody	
4th foot....................	Brown	Woody	
5th foot....................	Brown	Woody	

* The soils described in this table are the only ones in this article referred to by these numbers. Wherever "No. 1" appears it means the same soil. The same is true of "Town Line" or "Hudsonville," etc.

TABLE 5—*Continued*

SAMPLE NUMBER OR NAME	COLOR	TEXTURE	VEGETATION
Homer:			
1st foot....................	Dark brown	Finely divided	
2nd foot...................	Dark brown	Slightly woody	
3rd foot...................	Dark brown	Slightly woody	
4th foot...................	Dark brown	Slightly woody	
Thorpe:			
1st foot....................	Dark brown	Finely divided	
2nd foot...................	Brown	Slightly fibrous	
3rd foot...................	Brown	Slightly fibrous	
4th foot...................	Brown	Slightly fibrous	
Hudsonville:			
1st foot...................	Black	Finely divided	
2nd foot..................	Dark brown	Slightly woody	
3rd foot..................	Dark brown	Slightly woody	
Kingery:			
1st foot....................	Black	Finely divided	
2nd foot..................	Black	Slightly coarser	
3rd foot..................	Black	Slightly coarser	
Ingham County[1]:			
0–6 inches..............	Dark brown	Finely divided	
6–24 inches..............	Brown	Slightly coarser	
24–40 inches..............	Brown	Somewhat woody	
Ingham County[2]:			
0–15 inches..............	Dark brown	Finely divided	
15–36 inches..............	Brown	Somewhat coarser	
Posen:			
0–4 inches	Brown	Coarse	
4–24 inches..............	Brown	Coarse	
24–36 inches..............	Brown	Woody	
36–48 inches	Dark grayish brown	Fine, colloidal	

Additional studies were made with respect to the heat of wetting and unfree water of samples taken from the first foot of numerous deposits. The color, texture and vegetation are given in table 5. The data in table 4 show the relationship between the heat of wetting, the per cent of water that fails to freeze on the oven-dry basis, and loss upon ignition. The materials are arranged according to the ascending order of the per cent of water that failed to freeze. The heat of wetting and the loss upon ignition also are given.

TABLE 6

Moisture content and shrinkage of organic soil profiles

NAME OF DEPOSIT	DEPTH OF SAMPLE	WATER TABLE	WATER BY WEIGHT	WATER PER CUBE	APPARENT	SHRINKAGE
	inches	*inches*	*per cent*	*gm.*	*sp. gr.*	*per cent*
Thorp's..........	0–4		143.1	418.5	0.28	33.02
	12–16		384.4	673.5	0.17	50.50
	24–28		577.9	887.0	0.15	78.03
	30–34		692.7	906.8	0.12	70.47
	36–40		653.7	928.2	0.13	80.47
	48–52		556.8	907.1	0.15	61.41
Chandlers........	0–4		147.8	511.0	0.33	33.00
	12–16		466.5	833.5	0.17	68.36
	24–28	36	487.7	908.1	0.18	78.03
	36–40		860 6	947.5	0.10	75.87
	48–52		826.6	929.8	0.14	80.25
Trowbridge.......	0-4		110.6	460.0	0.40	23.09
	6–10		479.7	880.2	0.17	78.03
	12–16	30	616.2	901.3	0.14	78.03
	24–28		898.1	950.2	0.10	58.17
	36–40		1333.8	941.4	0.07	64.84
	48–52		1183.3	972.7	0.08	70.19
South Farm.......	0–4		126.1	320.5	0.24	33.0
	12–16		530.7	758.3	0.14	61.33
	24–28	30	555.5	864.3	0.15	69.05
	36–40		691.6	924.1	0.13	70.45
	48–52		742.5	939.2	0.12	61.33
Valleau...........	0–4		139.4	367.1	0.25	28.33
	8–12		392.2	663.5	0.16	63.16
	12–16		500.9	720.7	0.14	64.61
	24–28	72	748.6	792.7	0.10	56.30
	36–40		734.5	914.4	0.12	59.64
	48–52		933.2	951.8	0.10	56.30
	60–64		912.7	948.3	0.10	54.56
Shaw's..........	0–4		83.1	366.7	0.42	23.09
	6–10		274.9	654.9	0.23	50.50
	12–16		483.3	825.9	0.16	61.41
	24–28		719.1	931.2	0.12	84.19
	36–40		611.4	934.2	0.15	81.19
	48–52		325.0	886.0	0.26	78.03
Town Line........	0–4		82.3	335.5	0.39	33.00
	6–10		292.3	716.7	0.23	66.28
	12–16	39	401.8	829.2	0.20	73.19
	24–28		697.2	937.0	0.13	66.28
	36–40		744.5	965.6	0.12	83.90
	48–52		355.2	918.3	0.25	57.21

TABLE 6—*Continued*

NAME OF DEPOSIT	DEPTH OF SAMPLE	WATER TABLE	WATER BY WEIGHT	WATER PER CUBE	APPARENT	SHRINKAGE
	inches	*inches*	*per cent*	*gm.*	*sp. gr.*	*per cent*
	0–4		134.7	565.3	0.40	33.00
	6–10		246.2	698.8	0.27	46.37
	12–16		432.0	716.3	0.16	54.37
Farm Lane........	24–28		646.4	919.2	0.14	56.34
	36–40		675.6	925.6	0.13	56.34
	40–44		821.8	931.0	0.11	78.03
	48–52		1069.0	976.9	0.09	80.47

The results seem to show that the heat of wetting and the unfree-water-holding capacity of organic soils are dependent not entirely upon the organic content but upon the state of decomposition and nature of the materials. Soils 1, 2 and 3 have a very high organic-matter content and their heat of wetting and unfree-water-holding capacity are rather low, while 20, 13 and 17 are among those of lowest volatile matter content and have an unfree-water-holding capacity and heat of wetting slightly greater than those of 1, 2 and 3. Furthermore, soil 15, which has the highest unfree-water-holding capacity and next to the highest heat of wetting, has a very high organic matter content.

SHRINKAGE UPON DRYING.

The samples utilized for the accumulation of data on the volume weight and shrinkage upon drying were taken by excavating to the desired depth and sampling with a galvanized iron cube open on one side. The cube was carefully inserted into the various sections of the deposits, and removed, the contents weighed and oven-dried, and the measurements taken. The materials were collected August 1, at a time when the surface layers were not very high in water content. The results of these investigations are presented in table 6. A few of the cubes after drying are shown in plate 1.

It is to be noted that in nearly all cases the cubes taken from the surface layers practically retained their cubical shape on being dried. They shrank somewhat but the vertical shrinkage was about the same as the horizontal shrinkage. In case of the samples taken below the surface the horizontal shrinkage was less than the vertical. The greatest change in volume was found to take place in the layers of very fine and somewhat colloidal material, while a medium shrinkage occurred in the more fibrous layers. In addition, the vertical shrinkage in proportion to the horizontal shrinkage was greatest in the fibrous layers. The apparent specific gravity of the cubes as removed from the field was determined, and was found to be the greatest in case of the first section sampled.

SUMMARY

1. The amount of water an organic soil contains has some influence on the amount it will hold unfree, the latter being greatest where the water content is high. Air-drying a soil and wetting it again has no effect on the amount of water it will hold unfree, provided the soil is allowed to become thoroughly moist before the determination is made.

2. The physical condition of organic soils has a great influence on the rate at which they will take up water. A fine-textured organic soil that is removed from the deposit while wet and allowed to dry in large chunks will take up water very slowly. This is especially true of the lower horizons of fine-textured materials. This physical condition has no influence on the amount of heat generated on wetting but it does have an influence on the rate at which heat is developed.

3. There is a very close relationship between the heat of wetting and the unfree-water-holding capacity of organic soils. It seems, however, that the ability of organic soils to develop heat upon becoming wet and to hold water unfree is dependent not upon the organic content of the soil but upon the stage of decomposition and nature of the materials. A soil with a very low organic content, such as is found at or near the bottom of some organic deposits, naturally has a low heat of wetting due to its mineral content; but, as a rule, the sections near the middle of the profile where the organic content is highest give less heat of wetting than those at the surface where the organic content is somewhat lower, but is usually more thoroughly decomposed.

REFERENCES

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(4) McCOOL, M. M., VEATCH, J. O., AND SPURWAY, C. H. 1923 Soil profile studies in Michigan. *In* Soil Sci., v. 14, no. 2, p. 95–106.

PLATE 1

FOUR-INCH CUBE OF ORGANIC SOIL, AFTER DRYING, TAKEN AT DEPTH INDICATED BELOW EACH CUBE

The 4-inch cube sample is shown at the left in each figure.

FIG. 1. Cubes taken from Farm Lane deposit. Note depth of greatest shrinkage at 40–44 inches near the bottom of the deposit.

FIG. 2. Cubes taken from Thorp's deposit. Here a thin layer of fibrous material is found at 32 inches between two layers of colloidal material.

FIG. 3. Cubes taken from Shaw's deposit. The depth of colloidal material or of greatest shrinkage is found between 20 and 44 inches.

FIG. 1

THORP

FIG. 2

SHAW
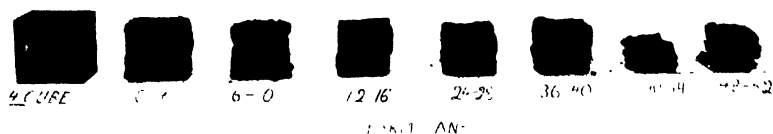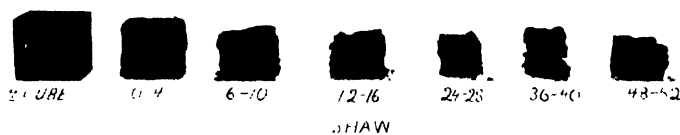
FIG. 3

NOTE ON THE ABSORPTION OF BASES BY SOILS

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It has for some time been regarded as an established fact that, all other things being constant, the greater the concentration of a base in solution the greater is the amount absorbed by a soil in contact with the solution. In a recent paper by C. P. Jones (1), however, it is claimed that beyond a certain concentration "an increase in concentration results in a decrease in absorption." As the mechanism of the absorption of bases by soils is so important and attractive a subject, it seems most desirable that such a challenge of a hitherto accepted fact of the problem as that made by Jones should be most carefully and critically considered. In this note, the writers wish to submit that Jones' deductions are invalid and that his experimental data cast no doubt whatever upon the accepted belief that the amount of base absorbed from solution by soils increases with concentration of the base.

Jones agitated solutions of suspensions of carbonates and bicarbonates of alkali and alkaline-earth metals with soil, and determined the amount of carbon dioxide liberated. The amount of carbon dioxide liberated was taken as a measure of the amount of carbonate decomposed and therefore of the amount of base absorbed. The following are his results with solutions of sodium carbonate and bicarbonate and an unlimed soil:

| Concentration of carbonate | Na_2CO_3 | | | | | | | | | | $NaHCO_3$ | |
	$0.01M$	$0.02M$	$0.03M$	$0.04M$	$0.05M$	$0.06M$	$0.10M$	$0.20M$	$0.50M$	Saturated	$0.06M$	$0.12M$
CO_2 from 10 gm. soil (mgm.)...	3.7	4.6	4.4	4.4	4.3	2.4	1.1	1.0	0.7	0.3	15.3	19.7

Now in the experiments with the normal carbonate, it seems obvious that the carbon dioxide formed by the reaction with the soil will not be wholly evolved as gas, but will react with the remaining carbonate to form bicarbonate. That carbon dioxide does so react with the carbonates of alkali and alkaline-earth metals is a familiar fact, and the conditions under which the carbon dioxide is formed in these experiments will clearly conduce to the quantitative attainment of the reaction. Also the greater the concentration of the carbon-

ate, the greater will be the tendency for the solution to retain the carbon dioxide. The falling off in the amount of carbon dioxide evolved as the concentration of the carbonate increases is held by the present writers to be due to bicarbonate formation and not, as Jones assumes, to a falling off in the amount of base absorbed and in the amount of carbon dioxide actually formed in the primary reaction. The far greater amount of carbon dioxide evolved when sodium bicarbonate was used (attributed by Jones to a greater hydrolysis of the bicarbonate) is in full accordance with this view.

Using as far as possible the technique described by Jones, the following experiments were carried out. The results support the criticism which is here submitted.

1. A slow current of air was drawn by means of a pump through 50 cc. of saturated potassium bicarbonate solution and thence into 50 cc. of saturated lime-water. A similar current was drawn at the same time by the same pump through 50 cc. of an equivalent solution of potassium carbonate and thence into 50 cc. of lime-water. After 2 hours it was found that the current passed

TABLE 1

Potassium absorbed by 10 gm. soil

SOIL	FROM K_2CO_3		FROM $KHCO_3$	
	Calculated from CO_2 evolved	Calculated from titration	Calculated from CO_2 evolved	Calculated from titration
	mgm.	*mgm.*	*mgm.*	*mgm.*
A heavy sour soil...................	0.30	33.40	43.90	40.40
A sour loam.......................	0.35	66.65	53.79	62.95
An acid-extracted soil..............	0.07	518.00	*	580.00

* The amount of CO_2 evolved here was more than sufficient to saturate the lime-water used.

through the bicarbonate had completely carbonated the lime-water, while that which had passed through the carbonate solution had carbonated only 1 per cent of the lime-water.

2. Fifty-gram portions of a sour soil were treated respectively with saturated potassium bicarbonate and an equivalent solution of potassium carbonate. The carbon dioxide evolved was collected in lime-water and estimated. Also the solutions were filtered at the end of the experiment, and the amount of base absorbed was estimated by titration. The results are given in table 1.

It seems abundantly clear therefore that the amount of carbon dioxide *evolved* when normal alkali carbonates react with soil is no measure at all of the amount of base absorbed.

REFERENCE

(1) JONES, C. P. 1924 Adsorption and absorption of bases by soils. *In* Soil Sci., v. 17, p. 255–273.

ALKALI SOIL INVESTIGATIONS: III. CHEMICAL EFFECTS OF TREATMENTS[1]

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Any treatment of alkali soils, as previously pointed out (6), must involve, among other things, the replacement of the bases in the zeolitic portion of the soil and the creation of a reaction favorable for plant growth. By improving the physical condition of the alkali soil, as outlined previously (5, 6), the leaching operations are facilitated. This in turn must have an effect on the replacement process, since the presence of large amounts of the soluble salts hinders the interreaction of the ameliorating agent with the replaceable zeolitic cations.

Table 1 gives the scheme of treatments used in the first series of experiments. Flower pots, of 1.4 pounds capacity, were used in studying the effects of various treatments in combination with leaching operations. Large earthenware glazed pots were used for studying the effects of the various treatments without leaching. The flower pots were paraffined to prevent absorption. It was found later that this treatment did not accomplish the purpose and some salts, especially potassium were absorbed by the clay walls.

From time to time a number of small pots were taken to the laboratory and leached. The purpose was to study the effects of the various treatments on the leaching capacity of the soil. At the same time analyses of the leachings were made to determine the changes produced by the treatments. In the series of experiments reported, tap water was used for leaching, with the thought that such water would correspond more closely to irrigation conditions. The procedure was as follows:

Each pot received a total of 400 cc. of water; the water was allowed to be in contact with the first two samplings (taken after 14 days and 48 days) for an indefinite period of time, and the rate of percolation was followed. Later a definite period of time, 48 to 72 hours, of contact was used, after which the water from the surface was poured off. The leachings were measured and then made up to 250 cc. In cases where the leachings amounted to more than 250 cc. they were made up to 300 cc.

Simultaneously with the leaching of the small pots, samplings were made from the large pots. Fifty grams of soil were mixed with 500 cc. of distilled

water, shaken occasionally for three hours, left over night, centrifuged for one and one half hours and analyzed in the same manner as the leachings.

Hibbard (4) has shown that water extracts do not represent the true condition in the soil. The displacement method which is supposed to represent the actual soil solution shows that carbonates, bicarbonates and phosphates

TABLE 1

Treatment of alkali soils, first series

LABORATORY NUMBER	TREATMENT
1	None
2	4000 lbs. sulfur
3	4000 lbs. sulfur + 5 tons peat
4	6000 lbs. sulfur
5	6000 lbs. sulfur + 5 tons peat
6	2000 lbs. sulfur
7	2000 lbs. sulfur + 5 tons peat
8	4000 lbs c.p. alum + 5 tons peat
9	4000 lbs. c.p. alum + 2000 lbs. sulfur
11	5 tons peat

TABLE 2

Analyses of leachings from pots incubated 14 days: first series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH	PARTS PER MILLION IN DRY SOIL								
		C as CO_3	C as HCO_3	C as organic carbon leached out as C*	Cl	Ca	Mg	P as phosphates	S as sulfates	N
	cc.									
1	188	27.8	107.6	84.9	2204.6	40.9	6.3	9.4	486.9	10.8
2	168	0.0	24.1	38.8	2184.9	114.9	8.3	11.4	604.6	5.6
3	160	0.0	23.6	118.4	2362.1	133.8	6.9	11.9	826.7	12.7
4	159	0.0	37.4	41.5	2440.0	111.8	5.8	11.4	776.3	7.8
5	195	0.0	29.4	170.8	2303.0	163.7	8.2	12.9	855.0	13.2
6	182	Traces	71.5	49.2	2365.2	53.5	3.9	12.9	677.1	9.3
7	175	0.0	67.7	182.9	2420.6	55.1	3.5	15.7	676.5	18.3
8	180	4.2	84.3	66.1	2244.0	36.2	2.8	3.6	659.8	9.3
9	225	0.0	49.1	154.0	2362.1	132.2	6.5	3.4	941.6	7.2

*Organic carbon was determined by subtracting the sum of carbonate and bicarbonate carbon from the total determined by the wet combustion method, with permanganate and sulfuric acid.

are over-estimated; thus the water extract considerably misrepresents the actual conditions in an alkali soil. The point is well taken, but solubility studies of the constituents would reveal exactly the same story. The extracts do not represent the true condition for the reason that the hydrogen ions of water as shown (6) have a high coefficient of energy of absorption

and they replace other cations. We should therefore expect that by replacing sodium with hydrogen more sodium carbonate and bicarbonate would be formed. The purpose of our analyses is to compare the effect of the products of sulfur oxidation and of other treatments on the exchange of ions in the alkali soils under uniform methods of experimentation. Taking the

TABLE 3

Analyses of alkali soil extracts after 14 days incubation: first series

LABORA-TORY NUMBER OF TREATMENT	PARTS PER MILLION IN DRY SOIL									
	C as CO_2	C as HCO_3	Cl	SiO_2	Ca	Mg	P as phosphates	Iron and aluminum as oxides	S as sulfates	Reaction
										pH
1	26.4	384.7	3500	.....	.....	.....	59.1	.....	608.0	9.0
2	Trace	200.3	3239	798	319.5	182.6	74.5	219.2	1025.0	8.0
3	0.0	188.1	3239	598	435.6	182.6	62.3	219.2	996.8	8.0
4	0.0	160.6	3497	159.6	420.2	213.2	34.8	338.8	1119.0	8.0
5	0.0	137.1	3497	478.2	459.6	174.0	57.2	139.5	1250.0	8.0
6	6.0	199.8	3239	438.5	379.8	139.2	56.4	338.8	952.2	8.2
7	5.9	251.0	3239	478.7	359.5	.....	.....	219.2	912.0	8.2
8	12.1	219.3	2990	217.9	299.8	147.8	69.7	259.0	874.0	8.2
9	0.0	148.6	3239	239.3	399.6	156.6	49.4	139.5	1217.0	8.0
11	6.0	375.1	3239	1275.0	459.6	174.0	54.1	949.8	594.9	9.0

TABLE 4

Analyses of leachings from pots after 48 days incubation: first series

LABORA-TORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH	PARTS PER MILLION IN DRY SOIL									
		C as CO_2	C as HCO_3	Cl	SiO_2	Ca	P as phosphates	K	Na	S as sulfates	Reaction
	cc.										*pH*
1	102	36.5	125.6	1984	3.8	24.6	17.0	117.6	1934	380.3	9.0
2	260	0.0	38.5	1866	20.8	191.8	10.7	100.0	2011	657.0	8.0
3	125	1.2	55.3	1984	11.3	113.5	5.0	.....	....	859.8	8.4
4	262	0.0	35.7	2055	31.2	185.2	6.9	117.2	2290	1092.0	8.0
5	312	0.0	31.1	2362	17.6	293.2	7.1	110.1	2486	1130.0	8.0
6	158	0.9	38.3	1653	12.3	88.8	8.3	93.5	1759	599.3	8.4
7	142	0.6	41.1	2614	14.2	85.0	11.3	98.7	2497	757.8	8.2
8	230	7.9	83.1	1960	10.4	37.8	14.8	159.7	1896	444.3	8.6
9	265	0.6	45.5	1866	9.4	154.0	7.7	138.4	2214	884.2	8.4
11	78	14.6	110.3	1771	14.2	32.1	11.3	70.4	1760	370.7	8.8

same amount of soil and water we get a picture of the transformations due to the treatment. The leachings aid in bringing out the details of the picture.

In comparing data of the leaching with that of the extracts the following is to be remembered. When a soil extract is made and then filtered through paper, the filtrate will as a rule be turbid if the particular soil has colloids,

as is the case with the alkali soils. However, the same soil when leached gives a perfectly clear liquid. The latter is nothing more than the filtrate

TABLE 5

Analyses of alkali soil extracts after 60 days' incubation: first series

LABORA- TORY NUMBER OF TREAT- MENT	PARTS PER MILLION IN DRY SOIL									
	C as CO_3	C as HCO_3	Cl	SiO_2	Ca	Mg	P as phos- phates	Fe and Al as oxides	S as sulfates	Reac- tion
										pH
1	15.7	371.3	1998.3	2133.7	479.5	335.5	40.4	1858.1	407.8	8.8
2	0.0	138.2	2121.1	398.4	601.5	196.0	48.0	499.1	1159.0	7.7
3	0.0	148.3	1499.1	377.9	601.5	248.8	52.9	299.9	921.2	7.2
4	0.0	139.2	......	198.4	640.9	213.5	50.5	239.3	1207.8	7.2
5	0.0	124.7	2373.1	359.0	741.7	227.7	51.4	359.0	2234.5	7.3
6	0.0	212.2	2617.2	338.5	439.6	196.0	....	299.1	1007.8	7.7
7	0.0	207.8	2373.1	557.4	479.5	226.7	50.5	459.8	1081.8	7.7
8	Traces	266.7	1499.1	359.0	419.6	234.6	52.9	259.8	511.7	8.6
9	0.0	139.5	2247.1	377.9	479.5	209.4	48.0	198.4	1373.1	7.3
11	9.8	381.0	1998.3	977.9	439.6	274.9	65.3	951.1	503.9	8.8

*Consider absorption by walls of various pots. Note the SiO_2 in alum treatment.

TABLE 6

Analyses of leachings from pots after 95 days' incubation: first series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH	PARTS PER MILLION IN DRY SOIL											
		C as CO_3	C as HCO_3	Cl	SiO_2	Ca	Mg	P as phosphates	K	Na	S as sulfates	N	Reaction
	cc.												*pH*
1	75	31.0	113.3	1770.0	11.3	18.8	11.1	4.25	94.9	1295.2	335.4	10.7	8.8
2	285	0.0	26.7	1330.6	26.4	151.1	30.5	1.73	110.0	1262.9	584.2	9.1	7.7
3	298	0.0	28.3	2210.9	29.2	198.8	45.6	4.25	111.9	1253.4	1162.9	11.0	7.6
4*	290	0.0	21.7	1307.0	41.5	203.1	59.5	1.88	47.2	1338.5	1083.4	8.9	7.4
5	293	0.0	24.2	1588.9	30.2	196.0	56.0	5.66	106.2	1272.3	1203.1	8.1	7.2
6	90	0.0	26.7	1818.7	9.4	64.2	27.8	1.10	77.9	1269.2	727.5	7.0	7.7
7	150	0.0	48.8	1620.4	17.9	81.3	26.9	2.83	102.5	1262.9	820.4	10.3	7.6
8	138	8.3	91.3	1384.1	73.6	35.9	17.3	9.29	81.7	1299.1	481.8	10.3	8.6
9	210	0.0	38.4	2527.4	12.2	96.3	42.5	.....	144.5	1195.2	1182.6	7.8	7.4
11	53	8.5	43.4	1218.8	16.0	21.7	10.2	4.40	68.5	1300.7	203.1	12.4	8.4

*The paraffin from this pot was destroyed and some of the salts passed through the walls. This will account for some discrepancies in the determinations; note the retention of K by the porous walls of the pot.

of the extract, differing only by the kind of filter used: in the extract the filter paper is the filter, while in the leachings the soil is the filter. In the latter case the mechanical absorbing capacity of the soil plays its part. The

data on the leachings furnish much evidence in this respect. Especially is this true in connection with the colloids such as the silicates. Tables 2 to 10

TABLE 7

Analyses of alkali soil extract after 95 days, incubation: first series

LABORA-TORY NUMBER OF TREAT-MENT	PARTS PER MILLION IN DRY SOIL										
	C as HCO₃*	Cl	SiO₂	Ca	Mg	P as phosphates	K	Na	S as sulfates	N	Reaction
											pH
1	457.7	3036.0	1758.0	218.8	270.5	56.6	321.0	3576.2	737.2†	105.8	8.2
2	122.8	2947.9	159.0	760.5	170.0	7.8	321.0	3963.6	1944.8	57.0	7.4
3	106.7	3746.3	149.6	760.5	213.5	....	370.0	4636.0	2015.6	67.7	7.3
4	75.5	2747.9	139.8	1281.8	253.0	6.2	321.0	4001.4	2459.7	40.9	7.1
5	80.4	3697.4	159.0	1160.5	327.5	9.4	352.0	5350.9	2988.8	45.6	7.0
6	160.1	3146.3	119.6	319.6	144.0	7.8	321.0	4065.9	1607.8	64.8	7.6
7	127.5	3398.2	119.6	603.1	182.6	15.1	272.0	4673.8	1935.3	40.9	7.4
8	308 4	3647.0	379.6	159.0	132.9	7.8	321.0	4550.9	1206.2	45.6	7.8
9	122.8	3697.4	69.2	530.6	177.9	7.8	321.0	4944.6	1889.6	37.7	7.6
11	453.5	3295.9	1199.9	190.5	151.0	58.2	352.0	3899.0	649.5	68.0	8.3

*No carbonates were present except in No. 11, which had some traces.
†Note extremely high sulfur content of control.

TABLE 8

Analyses of second* leachings from pots after 108 days incubation: first series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THORUGH	PARTS PER MILLION IN DRY SOIL									
		C as CO₂	C as HCO₂	Cl	SiO₂	Ca	Mg	P as phosphates	K	Na	S as sulfates	Reaction
	cc.											*pH*
1	80	2.1	42.5	814.1	29.2	8.2	10.2	3.36	26.6	363.7	57.8	8.8
2	165	0.0	15.7	979.4	15.1	105.0	30.0	2.33	66.4	763.7	366.9	7.4
3	190	0.0	12.3	413.5	26.4	133.8	32.5	2.33	39.6	442.5	275.2	7.6
4	270	0.0	10.5	873.9	24.5	251.0	66.4	3.35	59.8	598.4	570.0	7.4
5	275	0.0	8.5	212.5	20.7	200.7	44.4	2.34	48.3	371.6	423.6	7.4
6	186	0.0	34.3	1133.8	11.3	48.1	27.4	1.76	93.8	599.9	182.6	8.0
7	160	0.0	32.5	330.6	18.8	26.4	15.5	2.33	37.0	418.8	177.9	8.0
8	287	1.8	45.3	1215.6	7.5	236.6	17.6	2.92	102.0	730.6	114.9	8.8
9	156	0.0	17.3	779.4	4.7	46.9	14.8	1.90	75.9	470.8	192.1	7.6
11		1.6	58.2	708.6	137.0	15.1	19.3	3.77	60.7	377.9	60.0	8.8

*First leaching was made after 14 days incubation.

give the analyses of the leachings and extracts on the first series of experiments of alkali soils.

The data in these tables consist of two classes: one on the leachings, the other on the extracts. The first class gives the data on the actual amounts

of salts capable of being leached out. The second class presents the data on the changes which took place in the soils on account of the treatment. The extracts were prepared at the same time that the leaching operations were carried out. While not strictly comparable, because of the different conditions in the small flower pots and the large earthenware pots, the data

TABLE 9

Analyses of leachings from pots after 140 days incubation: first series*

LABORA-TORY NUMBER OF TREAT-MENT	AMOUNT LEACHED THROUGH	PARTS PER MILLION IN DRY SOIL								
		C as CO_2	C as HCO_3	Cl	SiO_2	Ca	K	Na	S as sulfates	Reaction
	cc.									pH
1	20	21.8	37.4	2759	1.57	6.2	77.1	1359.0	286.6	8.8
2	210	0.0	35.5	4063	15.1	227.3	333.8	2496.0	796.8	7.2
3	205	0.0	27.5	2669	15.1	141.0	166.9	1762.0	837.7	7.3
4	195	0.0	11.1	2231	16.0	195.1	155.7	1294.0	568.4	7.5
5	205	0.0	26.4	3270	18.8	174.1	190.5	2137.0	1008.0	8.0
6	110	0.0	24.0	2947	6.6	101.5	182.3	1795.0	585.8	7.7
7	205	0.0	38.7	2787	22.6	138.2	151.8	1629.8	626.7	7.6
8	145	0.94	28.6	2137	3.8	28.3	296.2	925.9	154.3	8.2
9	65	0.94	14.1	1677	.....	62.2	85.9	900.7	308.6	8.2
11	10	10.8	14.1	1315	5.5	11.8	92.4	568.4	77.1	8.4

*Some of the pots apparently absorbed some of the salts as indicated by the crust-like formation on the outside.

TABLE 10

Analyses of alkali soil extracts after 140 days incubation: first series

LABORATORY NUMBER OF TREATMENT	PARTS PER MILLION IN DRY SOIL				
	C as CO_2	C as HCO_3	Cl	Ca	S as sulfates
1	1.96	439.6	3050	340.8	601.7
2	0.0	58.0	2700	1443.6	1717.4
3	0.0	64.9	2700	1283.2	1695.6
4	0.0	32.5	2900	1984.9	2187.8
5	0.0	39.3	2400	1644.1	2133.1
6	0.0	131.8	2600	862.1	1312.7
7	0.0	118.0	2650	721.8	1285.3
8	Trace	283.2	2900	280.7	820.4
9	0.0	128.8	2800	501.2	1586.2
11	5.88	383.5	2850	340.85	574.3

on the leachings and extracts from the same incubation periods help to reveal the conditions existing and changes produced in the soil because of the treatments.

We shall take up the fate of the various elements and compounds in the extracts as they are influenced by the treatments.

CHANGES PRODUCED IN THE VARIOUSLY TREATED SOILS AS REVEALED BY
THE EXTRACTS AND LEACHINGS OF THE FIRST SERIES OF EXPERIMENTS

Reaction

After 14 days of incubation the oxidation of sulfur had proceeded far enough
to increase the hydrogen-ion concentration of the extracts very markedly.
The alum, because of its acid character, also increased the hydrogen-ion con-
centration of the extract; its power in this respect being equal to that of 2000
pounds of sulfur. After 60 days the reaction shift was still more noticeable
in the soils treated with sulfur. Even the 2000-pound application (table 5,
no. 6) shows a pH reading of 7.7 against pH 8.8 in the untreated culture.
On the other hand it is worth while to note that the alum-treated culture
(no. 8) has a pH reading of 8.6, very close to that of the control. Apparently
the buffers present in the soil have overcome the little acid present in the
alum. The possible reactions of the alum with reference to increase or de-
crease in hydrogen-ion concentration were discussed in the previous paper
(5, p. 401, also 6, p. 26). After 95 days of incubation a general shift of the
reaction towards the acid side was apparent. Even the control came to a
point where only traces of carbonates could be detected. The reason for that
shift could be explained only on the basis of displaced equilibrium. Again
the alum treatment without the sulfur showed practically no effect on the
reaction at this period of incubation. It is worth while to mention the
beneficial effects of the combined alum and sulfur treatments up to a certain
point in the incubation periods (no. 9) and the gradual disappearing of these
effects upon further incubation. It corroborates the data on the physical
effects (5, p. 402); the same explanation may be offered in this connection.

Turning our attention to the data on the leachings it will be noted that
the tendency of the reaction confirms the data on the extracts.

Another point worth mentioning is the effect of the peat on the reaction.
The changes produced do not warrant any definite conclusions. There is a
tendency towards less alkalinity; it may be due to the utilization of the Na_2CO_3
in the peptization of the organic matter.

Carbonates and bicarbonates

It has already been pointed out that the carbonates and bicarbonates in
the untreated cultures are not a constant value, the velocity of the reactions
changing from left to right and vice versa. For this reason we find the amount
of carbonates and bicarbonates shifting from time to time. On the other
hand, the treated cultures showed a progressive disappearance of the car-
bonates and bicarbonates. After 14 days of incubation the 6000-pound
sulfur treatment (no. 4 and 5) showed no trace of carbonates; over 60 per
cent of the bicarbonates also disappeared. In the case of the sulfur treat-
ment the sulfuric acid formed, which is the driving force of the reaction,
prevents reversion. One of the end products is carbonic acid which upon

decomposition may unite with the cations of the zeolitic portion of the soil and form carbonates again; however, in the presence of sulfuric acid the newly formed carbonates disappear again. The reactions may be expressed in the following equations:

(1) $R - CO_3 + H_2SO_4 = R - SO_4 + H_2O + CO_2$
(2) Replaceable cations $+ CO_3 = R - CO_3$
(3) $R - CO_3 + H_2SO_4 = R - SO_4 + H_2O + CO_2$
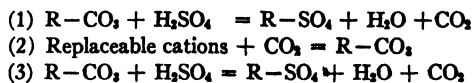
After 60 days, even with the 2000-pound application of sulfur, no traces of carbonates could be found and about 40 per cent of the bicarbonates disappeared. In general the rate of disappearance of the carbonates and bicarbonates is increased with the increase of sulfur. Unquestionably the physical improvement of the soils is largely due to the disappearance of the carbonates which peptize the colloids and thus bring into play all the objectionable features of colloids in alkali soils.

The influence of alum treatment on the alkali soil carbonates and bicarbonates illustrates again the contention that its effects are marked in the beginning, but gradually disappear. It will be noticed that after 140 days with the alum treatment (no. 8) only 30 per cent of the bicarbonates disappeared. The combined alum and sulfur treatment (no. 9) is not better than the sulfur alone. It will be recalled that from the standpoint of colloid coagulation the combined effect was greater in some cases than the arithmetic sum of either treatment. The peat treatment did not demonstrate any very marked changes in the combating of the carbonates or bicarbonates. Some decrease in the bicarbonates was the general tendency. As mentioned before the solvent power of the Na_2CO_3 on the peat apparently decreased the amount of bicarbonate. Another feature which should not escape our attention is the variation in adsorption of the various cations and anions at the different incubation periods. The variability of the total carbon as carbonates and bicarbonates at the various incubation periods may be explained on the basis of stronger adsorption at these various periods. The variations are not only true with the carbonates but also with the other cations and anions as shown in the tables.

The data on the leachings show that the bulk of the carbonates and bicarbonates in the alkali soils are retained. Only 20 to 30 per cent of the carbonates and bicarbonates are washed out by leaching. Of course in this first series the flower pot cultures used for leaching and the large earthenware pots used for extracts are not strictly comparable. As pointed out the flower pots absorbed some of the salts since the paraffin treatment did not fully prevent this.

Chlorides

The data on the chlorides in the extracts show that even chlorine, one of the most easily extractable anions, does not always behave in the same way. After 14 days we find that in some treatments the chlorides were held back.

A very strange phenomenon may be noticed after the 60-day incubation period (table 5).   Only two-thirds or less of the total chlorides present were extracted.   It is possible that the sampling was at fault.[2]   The data on the 90 and 145 days' incubation show no sharp variations.   The discrepancies may be explained on the basis of increased or decreased negative adsorption. Some of the variations may easily be ascribed to the deterioration of the paraffin coating of the pot, which facilitated absorption by the porous clay walls.   In general the treatments have little influence on the behavior of the chlorides in the soil.

The data on the leachings (tables 2, 4, 6, 9) show that the chlorides lend themselves to such treatment, e.g., they are not strongly adsorbed and may easily be leached out.   Even the control cultures with a relatively low leach- ing capacity gave up about the same amount of chlorides as the treated cultures.   With only 20 cc. of leachings·the control culture after 140 days (table 9) shows the same amount of chlorides as some of the treated cul- tures which leached through ten times the amount.

The peat treatment showed no influence whatsoever on the course of the chlorides either in the extracts or in the leachings.

Silica (SiO₂)

It has been pointed out (5) that one of the chief colloids present in alkali soils is the silica.   In the course of the work a number of difficulties have arisen in connection with the attempts to determine the SiO_2 in the extracts. The chief trouble was due to the failure of the methods to give constant results.   At times the extracts had more suspended colloidal material, at times less, although the same methods were used.   Of course soil colloids do behave in that way, but still many of the inconsistencies must be cred- ited to the imperfection of the methods.

On examining the data on the SiO_2 it will be noticed that large amounts appear in the extracts from the control culture.   The sulfur-treated cultures show only small amounts of silica in solution.   The decrease is undoubtedly due to the coagulation of the silica colloids.   The alum-treated cultures with or without sulfur accomplished just as good results as the sulfur treat- ments.   It is very probable that part of the aluminum united with the silica forming the insoluble aluminum silicates.   Again we must record the very insignificant rôle of peat in coagulating or adsorbing the silica colloids.

The leachings show that the SiO_2 is tenaciously held by the untreated soils, only very small amounts being leached out.   We must keep in mind the fact that the untreated cultures did not permit efficient leaching; even in the treated cultures the per cent of SiO_2 leached out is comparatively small.

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[2] The sampling of alkali soils is quite a problem due to the accumulation of the salts at the surface.   Generally the samplings were made by boring in several places with a brass tube. This method was found to be satisfactory when done before any salt crust could be seen on the surface.

The inconsistencies apparent from some data in the tables are due to the imperfection of the methods; the general tendency, however, is as outlined above.

Calcium

Even the water extracts of the control cultures contain some calcium. Although the extractions were made uniformly in the same manner, still the amount of calcium extracted was different at every extraction. The reason for this phenomenon may be found in the well known equilibrium displacement, which may occur in the system alkali soil—soil solution. The compounds which calcium forms in the alkali soil solution are, of course, problematic. From the nature of chemical reactions we should expect the calcium to precipitate. From solubility studies, we know that the most probable insoluble compound under the conditions would be $CaCO_3$. In 100 cc. of water only 0.00052 gm. of Ca as $CaCO_3$ may be found at room temperature while actually after 60 days the control cultures showed 0.00479 gm. of Ca in 100 cc. of extract. There was over nine times as much Ca in solution as could be if all had been in the carbonate form. Bicarbonate is of course not excluded; it is, however, more logical to assume the presence of gypsum, since the soil solution contains an abundance of sulfates; it is very likely that the sulfate and carbonate are found in a condition of displaced equilibrium with the sulfate in the lead. In 100 cc. of solution it is possible to have 0.0529 gm. of Ca as gypsum or about ten times as much as was actually found. However, in such analyses we must keep in mind the soil solution with its reaction power due to the presence of various salts on one hand and the small concentration of the solvent on the other. The soil solution of the alkali soils is rich in chlorides and it is possible that some calcium exists in alkali soil solution as chlorides. The oxidation of sulfur brings into solution more calcium; the amount increasing with the increase of sulfur application. The question arises: where does the calcium come from? That it is not present in the form of carbonates that became soluble with the oxidation of the sulfur may be deduced from the pH readings, also from the data on the magnesium, a discussion of which is to follow. The total carbonates present are not sufficient to take care of the calcium as carbonates. The explanation must be sought in the replacement process in the zeolitic portion of the soil due to the high coefficient of absorption of the hydrogen from the sulfuric acid.

With the advance of the period of incubation the ratio of calcium brought into solution to sulfur oxidized is narrowing. For the first 60 days the ratio of calcium to sulfur was about 1 to 5; after 95 days the ratio was about 1 to 2 and after 140 days it was 1 to 1 and even lower in the cultures with large amounts of sulfur. The narrowing of the ratio of calcium to sulfur indicates that with the increased period of incubation the efficiency of the hydrogen ions from the sulfuric acid as a replacing agent is increased. The

explanation is fairly simple; in the first period of incubation there are in the soil solution a number of compounds capable of reacting and, of course, these are first to be attacked by the sulfuric acid. When the compounds in solution [in our case the soluble carbonates and colloids mentioned (5)] have been acted upon, the hydrogen ions are free to react with the zeolitic portion of the soil which then plays its part in the replacement process. As a result we get more calcium replaced in the later periods. These reactions have to be considered in any of the quantitative studies of cation replacement, such as the Gedroiz method (2). It is strange that this careful investigator left out these reactions in his studies. It is very likely that at this point all of the zeolitic calcium was replaced. The question naturally arises whether such a course is desirable in this particular alkali soil? The replacement of the calcium with hydrogen brings about, what Gedroiz calls, an unsaturated condition, it forms a hydrous aluminum silicate; this condition theoretically forces the alkali soil to an acid condition. It is a question which is very closely connected with the possible influences of the composition of the irrigation waters and the salts coming up from the lower horizons. From the data on the sodium content of these soils it seems that such salts come from below to the surface horizon. Even though the sodium has not a high coefficient of adsorption, when present in large amounts it will eventually replace the hydrogen ions and form a sodium alkali soil, especially after all the sulfur has been oxidized. However, under the conditions existing in the soil solution with appreciable amounts of calcium, it is very likely that the calcium after having been first replaced by the hydrogen will get back first into the zeolitic portion and the sodium may be washed down again, since the soil will be permeable to water. When left alone at this stage the alkali will come back, since an accumulation of sodium salts will produce again a sodium saturated zeolite, but if the alkali soil colloids may be kept down by small applications of sulfur, the washing out of the sodium salts will keep the soil in good condition. Of course this mode of treatment is problematic and if applicable it is adapted only to this particular soil under investigation. The knowledge of the replaceable cations in the zeolitic portion is of prime importance.

The condition of the alkali soils under investigation as revealed by the calcium and other data may be summed up from the standpoint of the theories advanced by Gedroiz as follows: The presence of the calcium as the chloride is not desirable and the washing out together with the sodium salts brings about a favorable condition for the formation of calcium carbonate and sulfate in the soil; this comes about with the further replacement of the calcium and sodium from the zeolitic portion. When left alone the calcium, which has a higher coefficient of adsorption than the sodium, will tend to enter the zeolite again. This will be possible after the driving force of the reaction, the hydrogen ions of the sulfuric acid, cease to be in excess.

The presence of larger amounts of calcium in solution is beneficial from another standpoint. The calcium, as pointed out by the studies of Loeb (7) and Osterhout (8) counteracts other injurious influences; in this case the soluble sodium salts. After washing out the soluble salts, an addition of lime—preferably burned lime—will increase the driving force of the calcium ion and the zeolites will get back the calcium. At this stage the colloids will be coagulated through the combined action of the hydrogen which is to come from the unsaturated zeolite and the soluble calcium in solution. This will, as pointed out, facilitate the leaching out of the undesirable sodium salts, which have the tendency to increase the colloidal fraction of the soil.

When we examine the leaching data we find that on the average not more than about 15 per cent of the calcium was leached out. This is very significant: the rôle this calcium is to play in the soil solution, after the alkalinity has been destroyed and the soluble salts washed out, is very important, as pointed out above.

A glance at the analyses of the extracts and leachings show that the alum has no power of replacing the calcium: the alum extracts do not show more calcium than the control cultures. There is, however, the possibility that on account of the low hydrogen-ion concentration of the alum-treated cultures, the replaced calcium formed calcium carbonate and exists as such. The importance of the reaction in the replacement process has not been studied. Even Gedroiz overlooked this extremely important factor.

In table 8 we find the data on the second leachings; the figures on the calcium from these leachings show that there was practically the same amount of calcium as in cultures which have been leached for the first time at about the same period of incubation. This would seem to indicate that the calcium as shown in the data on the extract does not represent the calcium in the soil solution; it is rather the calcium soluble in the amount of water used for extraction. The leachings do not give the true value for the calcium in the soil solution; they only show the amount of calcium capable of being dissolved in the amount of water used in the leaching operations. This may be inferred from a comparison of the calcium leached out the first time (table 2) and that leached out the second time (table 8). If we only remember the leaching capacity of the cultures at the two different periods as judged from the number of cubic centimeters leached through, we can easily see that the amount of calcium is about the same in both instances. The dynamic nature of the system (soil plus soil solution) and solubility studies predict such behavior. This phenomenon has a bearing on the practice of leaching in the field. It would seem that one leaching would be sufficient, since the calcium continues to come out from the zeolites and since the sulfur continues to oxidize even without leaching. There is, therefore, no necessity of further leaching and thus wasting plant-food. Greaves, Hirst and Lund (3) point out among other things that the phenomenon of non-productivity noticed on alkali soils after leaching may be partially due to the lack of phos-

phorus. There may be other factors, however, which would favor a leaching at an early period first and another one at a later period.

The unusually high calcium content in the second leaching of the alum-treated culture (no. 8) is very peculiar. It is the only case where the alum shows such a high replacement power. It may be argued that after leaching the calcium had a better chance to come out from the zeolitic portion. It seems as if the presence of the alum prevented the replacement of the calcium. This, however, has still to be proved.

Magnesium

A critical examination of the magnesium in the extracts seems to show that this particular soil has not much if any replaceable magnesium in the zeolitic portion. In other words this alkali soil is not a magnesium alkali soil, following the nomenclature of Gedroiz. The slight increases of the magnesium content in the extracts are insignificant as compared with the calcium increases as the period of incubation is advanced. The leachings show that only very little of the magnesium is washed out. The fact that the magnesium content does not increase even in the cultures with the highest amount of sulfur seems to show that it does not exist as the carbonate. It also suggests the same condition for the calcium.

Phosphorus

The data on the phosphorus do not throw much light on the subject. The oxidation of the sulfur seems to put the phosphates into an insoluble state. Apparently, the organic material as it is dissolved by the soda, carried much organic phosphorus. As the colloids are coagulated and the peptization of the organic matter by the soda ceases, the phosphorus content is decreased. The alum does not show any variations in the phosphorus content, except in the first period of incubation (14 days). The coagulation effect of the alum at this time is responsible for the diminution of the phosphorus in solution. It could not be the interaction of the aluminum with the phosphates, since the latter exist in organic form.

Sodium

We are to consider the element which is generally looked upon as the chief injurious agent in alkali soils. It has been shown already that according to the most recent knowledge on the subject of alkali soil formation the origin of such soils is to be sought for in the replaceable cations of the alumino-silicate complex known as zeolites. The salinizing process which may take place in one or more horizons of the soil profile for one or more reasons saturates the zeolites with some cation and this cation determines the nature of the alkali soil. It may also happen that two cations are responsible for the process. This salinizing process is followed by a desalinizing period at and

after which the soda appears; the appearance of the soda indicates that some sodium may be present in the zeolitic portion. As stated above this does not exclude any other cation. From the data on the calcium it was concluded that the soil under investigation was saturated with calcium in the zeolitic portion; thus the soil is undoubtedly partially a calcium alkali soil.

The data on the sodium from the extracts of the first series are available for one period of incubation only; still the reactions may be well inferred: there is an increase in the sodium content of the extract amounting to 50 per cent in the 6000-pound sulfur application. It is a great deal less in the other treatments. We can safely infer, however, that there is an increase in the sodium content with the advancement of the incubation period. Therefore, it seems that at least in its make-up the soil under investigation is not a purely sodium alkali soil. The presence of the large amounts of soluble sodium may be due to the fact that this soil is in process of desalinizing accompanied by the formation of soda, or more likely just the reverse may be true, i.e., the sodium is just beginning to invade the soil.

The data on the leachings show that sodium is leached out in appreciable amounts. Fifty per cent or more of the sodium is leached out with the first leaching operation. The figures in the first series are not so reliable since the walls of the clay pots have undoubtedly absorbed considerable of the soluble compounds.

Potassium

The potassium as revealed in the data is not of any great moment in the alkalinity of the soil investigated. The oxidation of sulfur does not increase the amount of potassium in the extract; apparently there is no zeolitic potassium to be replaced. The leachings show that potassium is not held back in this soil.

Sulfur

The initial high concentration of sulfates did not prevent the oxidation of the added sulfur. This may be judged from the data on the sulfates in the extracts. The rate of oxidation has been given in a previous paper (6) and need not be repeated here. In general it will be noticed, that with the higher applications of sulfur the advantages gained by the exchange of cations in the zeolitic portion are greater, e.g., more of the replaceable cations are forced out. As already mentioned it is the hydrogen ion of the sulfuric acid formed that is responsible for the replacement, having a high coefficient of adsorption. As the sulfates increase, the chances for the formation of gypsum and sodium sulfates (provided our supposition of the calcium-sodium alkali soil is correct) rather than calcium carbonate and sodium carbonate, are also increased. In any alkali soil the advantage of the presence of sulfuric acid consists in the combination of the sulfate radical with the replaced cations, preventing the formation of carbonates. The reactions involved

were given in the section on the carbonates and bicarbonates. Mention should be made of the reactions taking place in solution before replacement takes place. As pointed out (see p. 140) the replacement brings out cations which may combine with the CO_2 from the decomposition of the original carbonates present and other sources such as soil, air and decomposition products of the soil microbial flora. The distinct advantage of the sulfur as compared with gypsum lies in the formation of carbonic acid which is easily broken down as may be seen from the equation (see p. 140). When all of the replaceable cations are out from the zeolitic portion we should have an unsaturated soil, i.e., one which has replaced in the alumino-silicate complex all the replaceable cations by hydrogen.[3] Such a soil should be a true acid soil, but it is questionable whether it would be desirable to bring about such a condition. From the data on the second leachings (table 8, no. 6 and 7) we are justified in assuming that the 1-ton application of sulfur is not sufficient to replace all the cations in the zeolitic portion. The reaction of these leachings shifted back towards alkalinity, indicating that after the excess of the soluble sodium salts has been washed out by the first leaching more of the replaceable cations left the zeolitic portion, to form carbonates. Since all the sulfur has apparently been oxidized there was no more sulfuric acid to react with the carbonates. The reduction of the amount of soluble sulfates allows the formation of the carbonates.

A clearer understanding of this phenomenon will be brought out when we analyze the data on the second series.

The data on the leachings are significant inasmuch as they show that as soon as the colloids are coagulated and leaching operations are facilitated 50 or more per cent of the sulfates are leached out.

Nitrogen

The soil under investigation is poor in nitrogen, the total content being 0.0479 per cent. It is rich in nitrates and the soluble nitrogen is thus fairly high, amounting to about 25 per cent of the total. The action of the sulfur is to decrease the amount of soluble nitrogen in the extract. The decrease is undoubtedly due to the coagulation of the organic colloids which are rich in nitrogen. The leachings seem to carry much of the soluble nitrogen and

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[3] The theory of base exchange as outlined for the zeolites through the replacement of their cations by the hydrogen-ions of the sulfuric acid *presents a new aspect of soil acidity*. We may picture it as follows: a soil becomes acid when its zeolitic portion (the portion capable of exchange) is saturated with hydrogen, and there are no more basic substances to be replaced and come out in solution. Only then will free acids (mineral or organic) or acid salts appear in the soil solution. Uutil then no real acidity, i. e. free acids, is possible. The zeolites partially saturated with hydrogen may show acidity when treated with neutral salts. In this case the replacement process described in this paper takes place; in other words, the cation of the neutral salt replaces the hydrogen. These considerations have been suggested in the course of the alkali soil investigation and are now being looked into.

the losses should be taken care of when the soil is ready for cropping. The best forms of nitrogen to apply would be the organic forms and ammonium sulfate. Experimentation in this direction will determine the best method of procedure.

Peat

In analyzing the behavior of the various cations and anions in the differently treated alkali soils, mention was made of the influence of peat in alkali soil treatment. The peat did not have any striking effects. In general it would be expected that the humates and the cations combined with them would react with the cations present in solution and thereby have an effect on the replacement process in the zeolitic portion and also on the general shift of the cations. It is known that the cations in the humates are in loose combination. Examining the tables on the extracts and leachings one may note that up to the higher periods of incubation the calcium is greater in the cultures treated with peat in combination with sulfur. The reverse is true with the alum treatment and peat, or the peat alone. The authors suggest the possibility of replacement of calcium in the humates by hydrogen from the sulfuric acid augmenting the total amount of calcium.

Gedroiz (1) stresses the point of similarity between the cations of the zeolites and the humates, and the facts on hand are in accord with the theory. As the period of incubation advances there is apparently no more calcium to replace. On the other hand, alum treatment with peat and the peat alone apparently caused none of the calcium to be replaced. If the course of reaction with the peat as outlined is true, then there is some advantage in adding the peat. Moreover, the peat serves as a buffer taking up some soda, reducing temporarily the alkalinity. This may be noticed from the data on the carbonates.

SUMMARY

In summing up the result of the first series of experiments this may be said: the 2000-pound sulfur treatment is not sufficient to bring about a complete transformation of the alkali soils. The sum total of hydrogen ions from 2000 pounds of sulfur available for replacement of the zeolitic cations and neutralization of the existing and potential soda is not sufficient. The alum has some merit, especially in combination with sulfur. This point will be discussed more fully when the second series of experiments is taken up.

The evidence on hand seems to point to the calcium-sodium character of the particular alkali soil under investigation. The soil is probably in process of desalinizing or more likely in process of formation. These postulates are based on the theories advanced by Gedroiz.

In the next and last paper the data on the second series of experiments will be taken up; the results of the effect of the treatments on some of the biological activities will be brought out; and also some vegetation experiments will be reported.

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[4] *See also* Loeb's books and publications in the Journal of General Physiology since 1918.

[5] *See also* Osterhout's numerous papers in the Botanical Gazette since 1906; in the Journal of Biological Chemistry, Science and other publications.

SECULAR AND SEASONAL CHANGES IN THE SOIL SOLUTION

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In a recent paper we have shown that solutions obtained from soils by a process of water displacement have many of the properties which the true soil solution should possess (2). Briefly stated:

a. The freezing-point depressions of such solutions are approximately equal to those obtained by direct determination upon the soils from which they are respectively derived when the soil displaced contains relatively large amounts of water (i.e., amounts optimum for plant growth).

b. Successive increments of solution from a given displacement have equal concentrations of electrolytes up to the point where dilution by the displacing water occurs.

c. There is an inverse relation between the concentrations of total electrolytes and of some of the individual solutes in the solutions obtained and the initial moisture contents of the soil as packed in tubes prior to displacement.

d. Concentrations of solutes in the displaced solutions are the same as those computed from water extractions for those constituents for which water extraction is a valid criterion (i.e., for substances—nitrates and chlorides—which are presumably always completely dissolved in the water of the soil when the latter contains amounts of water adequate for plant growth).

e. Concentrations of solutes in the displaced solutions are generally lower than those computed from water extractions for those constituents for which water extraction presumably gives too high results (i.e., for substances which are presumably present in part in the solid phase).

The above-stated facts and relations leave little doubt that such displaced solutions are substantially identical with the true soil solution of soils containing considerable moisture (conventional optima for plant growth). A difficulty presents itself, however, with respect to soils containing small amounts of water. Thus, while we have found, as stated above, that the freezing-point depression determined directly upon the soil is approximately equal to that of the displaced solution at high moisture contents, a similar agreement is not obtainable in soils at a low degree of moisture. It is therefore evident that either the freezing-point depression or the displaced solution from soils containing small amounts of water is defective as a measure of the soil solution. We have shown, however, that there is an inverse relation between total concentrations of electrolytes in the displaced solutions and the initial moisture contents of the soil. This latter result is what we should expect if all of the water of the soil is effective as a solvent and if no solutes are removed from the

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liquid phase by a decrease in the moisture content of the soil. Other evidence indicates that while there is some removal of solutes from the liquid phase with decreased moisture, such removals are relatively so small as to have little effect in disturbing the inverse relation of total concentration and moisture content. This relation and the agreement in freezing-point depression of displaced solution and soil at high degrees of moisture suggests an equivalence of the displaced solution and the true soil solution at body high and low moisture contents. The discrepancy between the freezing-point depression of the soil at low moisture contents and that of the displaced solution, deprives us of the evidence which would tend to make conclusive the proof of an absolute identity of displaced solution, and soil solution but does not negative such a conclusion. Rather do the facts suggest that the discrepancy is due to the inadequacy of the freezing-point depression made directly on the soil at low moisture contents as a measure of the concentration of the soil solution.[1]

Much other evidence, based upon careful studies of the qualitative and quantitative composition of displaced solutions and water extracts, tends to confirm our general conclusion. A theoretical difficulty presents itself in that it is impossible to conceive of such a thing as a physical partition between liquid and solid phase without disturbing the equilibrium as it exists in the soil. Even so, it by no means follows that changes in the liquid phase during the process of displacement are of substantial magnitude. In the light of all of the facts, the writers are of the opinion that the differences in total concentration and composition of electrolytes in the true soil solution from those of displaced solutions which satisfy certain criteria we have set up (2), are so small as to be without significance in terms of the capacity of the soil to produce crops.

Assuming the adequacy of the displaced solution as a measure of the true soil solution, it is evident that we have at our disposal a more accurate means of ascertaining the condition of the soil and the effect of environmental conditions upon its soluble matter, than has hitherto been available. The opportunity is thus presented of confirming in a definitive manner the conclusions based upon the results of water extractions (6) and of extending our knowledge by the measurement of those changes in the soil which are otherwise imperceptible. If our assumption is correct, it should, for example, be an easy matter to confirm substantial variations in the displaced solutions obtained from cropped soils at the beginning and end of a period of years and even of a single season, thus measuring the effect of crop withdrawals and other factors upon the soil solution.

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[1] The discontinuous character of the soil film in soils of low moisture content has, for some time, appeared to the writers as the indirect cause of freezing-point aberrations in such soils. Recently, through the courtesy of D. R. Hoagland, we have learned of certain verbal suggestions of E. A. Fischer which appeal to us as affording a reasonable explanation of such aberrations.

Since the importance of the displaced solution has only recently become recognized, it is obvious that sufficient time has not elapsed to permit of the accumulation of the evidence as to changes in displaced solutions obtained from a single mass of soil over a period of years. We happen, however, to have at hand a number of different soils collected in 1915, each of which was, at that time, made physically homogeneous by sieving and mixing, and then divided into three large (1800-pound) portions. Each of these portions has been continuously maintained under different conditions of treatment for 8 years.

One portion of each soil has borne a crop of barley every season; one portion bore a crop the first year (1915), but has lain fallow during all succeeding years; and the third portion has been kept in the air-dry condition and stored in tightly covered bins for the entire period. The justification for presenting this paper and for its title is the belief that the air-dried portions of soil have remained practically unchanged and that the data recently obtained from solutions displaced from such portions represent the condition of the soils from which they were respectively derived at the time they were first assembled.

If this is true, it is evident that we may legitimately compare the data recently obtained by displacement from the various portions of each soil to determine the effect of time and cropping upon its qualitative and quantitative composition. For convenience, we shall refer to the portions of soil which have been continuously cropped as "Cropped Soils (A)": to those which were cropped in 1915, but which have subsequently lain fallow as "Fallowed Soils (B)"; and for the portions kept in closed bins as "Air-Dry Stored Soils (S)."

All soils were sampled and displaced, and the displaced solutions analyzed in the spring of 1923. At the time of sampling both the fallowed and stored sets of soil were very dry and it was of course necessary to add water and permit the soils to come into equilibrium therewith before conducting the displacements. The cropped soils (A) had had the maximum opportunity to recuperate from the effects of crop withdrawals during the preceding season. The differences observed in the displaced solutions of these soils from those of their fallowed and air-dry duplicates, may reasonably be ascribed to the treatment (i.e., cropping) for the entire 8 years and not to seasonal variation. The effects of seasonal variation are shown by other data presented hereinafter.

The data for the 8-year period are given in table 1.

It will be observed that the moisture contents of the fallowed and stored portions are fairly uniform for each soil, but that the cropped portions were for the most part displaced at considerably lower moisture contents. Since the concentration of displaced solutions varies with the initial moisture content of the soil, only the most general comparisons can be made from the original data without allowance for the effects of the different moisture contents of the cropped soils. Such a calculation to uniform moisture content involves the assumption that the concentrations of each constituent are in an exact inverse proportion to the moisture contents of tne soil, which is not strictly

true. Hence it is desirable to bring out a few facts from the original data before making the conversions necessary to the further discussion. The limitations of the calculations to uniform moisture content will be discussed in their proper place.

TABLE 1

Displaced solutions from cropped (A), fallowed (B), and air-dry' stored (S) soils after 8 years

SOIL	MOISTURE	pH	PARTS PER MILLION OF DISPLACED SOLUTIONS										
			NO₃	HCO₃	Cl	SO₄	PO₄	SiO₂	Ca	Mg	Na	K	Total*
	per cent												
7A	10.7	7.4	174	83	0	655	1.1	—	283	106	49	24	1375
7B	16.8	7.6	1696	73	52	432	1.2	—	640	128	71	36	3129
7S	16.0	7.2	1468	69	313	184	3.3	38	547	112	123	39	2896
8A	9.6	7.4	274	93	0	633	2.5	—	267	93	31	20	1414
8B	15.1	7.0	1746	59	40	432	4.0	—	573	155	66	75	3150
8S	14.7	6.9	2182	77	260	451	7.2	61	539	204	156	156	4093
9A	11.4	7.6	160	73	0	432	0.9	—	213	75	27	12	993
9B	15.4	7.6	947	63	36	420	1.2	—	460	93	53	29	2102
9S	15.1	7.3	680	46	372	184	2.9	33	380	75	88	21	1882
10A	13.9	7.2	230	40	0	360	1.2	—	187	145	23	33	1019
10B	18.0	7.0	1704	34	32	348	2.1	—	547	136	47	74	2924
10S	18.5	6.8	937	34	348	148	4.0	51	360	91	115	89	2173
11A	12.9	8.2	166	160	0	645	3.3	—	213	93	84	39	1403
11B†													
11S	15.5	7.8	1049	171	367	344	12.1	49	407	128	203	100	2830
12A	12.1	7.3	115	40	0	281	2.3	—	120	46	27	13	644
12B	14.8	7.0	1503	34	40	337	0.3	—	585	151	60	45	2755
12S	15.1	7.3	208	39	80	170	3.1	48	145	48	52	30	823
14A	18.0	8.0	146	107	0	295	1.3	—	140	47	56	45	837
14B	17.9	7.4	1766	54	60	397	1.7	—	547	139	85	118	3168
14S	18.5	7.4	779	78	100	188	4.3	54	290	91	74	89	1747

* Sum of determined solutes.

† Soil not available for study.

The reader will observe from an inspection of table 1 the more obvious effects due to the different conditions under which the soils have been maintained and to the effects of cropping. Briefly, the concentrations of total electrolytes, of nitrates, and of several of the individual ions are, for the most part, materially decreased by cropping for a series of years, and increased by fallowing. Soil 8 constitutes an exception in that fallowing apparently has caused a decrease in concentration. This soil, however, has the highest con-

centration of any which we have studied, and the changes observed therein probably represent a type of effect characteristic of soils in a high state of fertility, in that stimulation of biological activities due to the treatment may result in diminished concentrations. Such an effect is consistent with field results with soils which do not respond to fallowing by increased production. Indeed, the stimulation of biological activities induced by too intensive, mechanical treatment in the processes of plowing, harrowing, and cultivation, are well known to be unfavorable to many sandy soils in the arid region. This result is variously ascribed to oxidation of organic matter, loss of nitrogen, and decrease in moisture-holding power, but it may also be in part caused by, or attended by, diminished concentrations of certain constituents of the soil solution.

CALCULATION TO UNIFORM MOISTURE

Since our previous studies of several of the soils used in the present work show that the concentrations of total electrolytes, nitrates, chlorides, and in these soils calcium, in the displaced solution, appear to vary inversely with the moisture contents of the soils, we may compute the approximate concentrations which would have been present in the displaced solutions from the "A" soils, had these been obtained at the same moisture contents as those of the "B" or "S" soils. However, we have also shown in previous work that this inverse relation does not hold exactly with reference to certain ions. Thus, when the moisture content of the soil is doubled, the concentration of the potassium ion in the displaced solution is somewhat more than half that obtained from the soil at the lower moisture content. In such calculations involving the potassium ion, the figures obtained, therefore, will be somewhat lower than the truth. They will represent minima which approach the truth to the extent to which the inverse relation holds, or, stating it another way, to the extent to which solid-phase potassium enters the solution when the moisture content of the soil is increased. The data of table 2 are of interest in this relation.

Such great percentage variations require that data to which they apply shall be interpreted with caution. It will be shown later (table 3), however, that the potassium-ion concentrations in the fallowed or air-dry soils are in no case less than 100 per cent greater and are frequently two, three, or four times as great as those of the cropped soils. Such differences are clearly due to the treatment of the soil and are not assignable to the inadequacy of the moisture correction.

We have also observed heretofore that the magnesium ion in our soils behaves in general like the potassium ion, so that the figures corrected for moisture will likewise represent minima. No study has yet been made of the sodium ion in this relation, but it is highly probable that any cation may, in part, be removed from solution by the reduction of moisture in the soil. In this case, also, we may, therefore, assume that the corrected figures represent minimum

TABLE 2

Potassium ion in displaced solutions at various moisture contents of soil as determined and as calculated

	SOIL 8		SOIL 9		SOIL 11	
	Moisture		Moisture		Moisture	
	per cent	*p.p.m.*	*per cent*	*p.p.m.*	*per cent*	*p.p.m.*
Determined..............	7.3	250	7.5	130	8.0	165
Calculated..............	14.6	125	15.0	65	16.0	83
Determined..............	14.8	150	14.3	85	16.6	140
Approximate variation..	−17 per cent		−24 per cent		−41 per cent	

TABLE 3

Displaced solutions from cropped (A), fallowed (B), and air-dry stored (S) soils after 8 years
(Results from table 1, calculated to a uniform moisture basis for each soil)

SOIL	MOISTURE	pH	PARTS PER MILLION OF DISPLACED SOLUTIONS										
			NO₃	HCO₃*	Cl	SO₄	PO₄*	SiO₃	Ca	Mg	Na	K	Total
	per cent												
7A		7.4	116	83	0	438	1.1	—	189	71	33	16	947
7B	16	7.6	1781	73	55	454	1.2	—	672	134	75	38	3281
7S		7.2	1468	69	313	184	3.3	38	547	112	123	39	2896
8A		7.4	179	93	0	413	2.5	—	174	61	20	13	955
8B	14.7	7.0	1798	59	41	445	4.0	—	590	160	68	77	3242
8S		6.9	2182	77	260	451	7.2	61	539	204	156	156	4093
9A		7.6	121	73	0	326	0.9	—	161	57	20	9	750
9B	15.1	7.6	966	63	37	428	1.2	—	469	95	54	, 30	2144
9S		7.3	680	46	372	184	2.9	33	380	75	88	21	1882
10A		7.2	173	. 40	0	270	1.2	—	140	109	17	25	775
10B	18.5	7.0	1658	34	31	339	2.1	—	532	132	46	72	2846
10S		6.8	937	34	348	148	4.0	51	360	91	115	89	2173
11A		8.2	138	160	0	537	3.3	—	177	77	70	32	1200
11B†	15.5												
11S		7.8	1049	171	367	344	12.1	49	407	128	203	100	2830
12A		7.3	92	40	0	225	2.3	—	96	37	22	10	524
12B	15.1	7.0	1473	34	39	330	0.3	—	573	148	59	44	2701
12S		7.3	208	39	80	170	3.1	48	145	48	52	30	823
14A		8.0	142	107	0	287	1.3	—	136	46	54	44	817
14B	18.5	7.4	1709	54	58	384	1.7	—	529	135	82	114	3069
14S		7.4	779	78	100	188	4.3	54	290	91	74	89	1747

* Bicarbonate and phosphate remain as in table 1 (see text.)
† Soil not available for study.

values. Preliminary studies of the behavior of the sulfate ion also indicate that a portion of the sulfate in some soils is removed from solution at diminished moisture contents; the computed figures, therefore, also represent minima.

In the case of phosphate, all of the evidence from displaced solutions and water extracts indicates that equilibrium of liquid- and solid-phase phosphate is established very rapidly so that changes in the moisture content of the soil do not appreciably change the phosphate-ion concentration. Thus phosphate concentration is independent of moisture content and no correction is necessary for this ion. The fact that bicarbonate is a weak ion and tends to form relatively insoluble carbonates suggests that its behavior should be more like that of phosphate than of any other ion. We should, therefore, anticipate that increasing the amount of moisture would not greatly decrease the concentration of this ion. A careful study of one of our soils (no. 12) gave 73 and 61 parts per million of the bicarbonate ion in the solution obtained by displacement when the soil contained respectively 7.4 and 15.0 per cent of moisture. The conventional correction for moisture content would, in this case, have given results so far from the truth as seriously to vitiate conclusions drawn from the data. Since the correction is inapplicable, we have merely repeated the original figure for bicarbonate in the corrected tabulation. The figures for bicarbonate in the "A" soils (table 3, see also table 5) therefore represent maxima.

EFFECT OF 8 YEARS' FALLOWING[2] ON DISPLACED SOLUTIONS

(Comparison of results from fallowed "B" with stored "S" soils continuously maintained in the air-dry condition for 8 years)

In five out of six cases, the total electrolytes and nitrates in the displaced solutions are substantially higher in fallowed soils than in the stored soils. In the case of soil 8, an exceptionally productive soil (as shown by crop records from the cropped duplicate for the first two years), there is a falling off in total concentration of displaced solution in the fallowed portion. The one exception, the causes of which are readily accounted for (page 155) does not weaken the conclusion that soils in general tend to have increased concentrations in their displaced solutions, if they are allowed to remain uncropped under conditions somewhat favorable to biological activity (aeration, moisture, etc.). It can hardly be doubted that under such circumstances, there is an increased concentration of the soil solution and that this result is an important cause of increased productiveness when such soils are eventually cropped.

[2] The so-called fallowed soils were actually cropped the first year and cultivated and watered the first 4 years. The remaining 4 years, they received no treatment other than weeding. Strictly speaking, therefore, the soils were not fallowed in the sense in which the word is used in field practice. We have deemed it necessary to use the term as being more nearly descriptive of the treatment as a whole than that supplied by any other abbreviated expression.

When we consider the effect of the treatments upon individual ions, it is obvious that these must, in general, follow the total concentration. Inspection of the results shows that the five soils which have increased total concentrations due to fallowing, have markedly increased in nitrate, sulfate, calcium, and magnesium.

In all cases, where data are available, the chloride ion not only diminishes, but tends, comparatively speaking, to disappear. Since chloride should always be present in the liquid phase, except when very high concentrations are involved, the cause of loss of this ion is not at first obvious. It should be recalled, however, that the "B" soils which we are calling fallowed soils for the period as a whole, were, in fact, cropped for the first year (see footnote, p. 157). The results of numerous investigations in this laboratory and elsewhere testify to the ease with which chloride may be absorbed by plants and thus removed from soils (4). It seems fair to conclude that the one crop grown on the so-called fallow soils has caused the effect observed. It should be noted in this connection that after 8 years' cropping ("A" soils), all chloride had been removed from all soils.

EFFECT OF 8 YEARS' CROPPING ON DISPLACED SOLUTIONS

(Comparison of results from cropped "A" soils, with fallowed "B" soils and with stored "S" soils continuously maintained in the air-dry condition)

The extraordinary falling off in concentration of total solutes and nitrates in the displaced solutions from the cropped soils is at once evident. With one exception (magnesium in soil 10), which we have reason to believe from other data represents an erroneous determination,[3] all of the cations are lower in the displaced solutions from the cropped soils than in those from the stored soils by what appear to be significant and in most cases by very substantial amounts. That such differences reflect and measure with considerable accuracy the changes which have taken place in the soil solution can hardly be doubted. The greatly diminished crops which have been taken from the soils during the latter years of the experiment are consistent with, and in our view, largely caused by these changes.

Two features of the changes due to cropping deserve special comment, viz., the decreases in phosphate concentration and the increases in sulfate. The phosphate results, in so far as we are aware, are unique in that they represent fairly accurate measurements by a rational procedure of changes in the concentrations of this ion in soils. With the exception of phosphate in 12B,

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[3] This discrepancy and the one noted in the following paragraph with reference to phosphate was not discovered until our solutions were exhausted. The first is unimportant for the purpose of our present discussion. The second if literally interpreted involves an unfortunate variation from a general type of behavior. Since phosphate behavior in soil is now undergoing special examination in this laboratory it was not deemed necessary to repeat the work on this soil for present purposes.

which may be erroneous,[4] the results are absolutely consistent, the stored soils having the highest, the fallowed next highest, and the cropped soils the lowest concentration, respectively.

The interesting question arises as to whether the diminished phosphate concentrations in the cropped soils are due to withdrawals by the plant or to some other cause. As stated repeatedly in the publications of this laboratory and as is obvious from any rationa lconsideration of the chemical properties of phosphates, as well as from the results of the extraction of phosphate from soils by varied proportions of water, it is clear that phosphate tends to form a saturated solution with respect to any particular physico-chemical system. Moreover, if from any cause (such as dilution), the phosphate concentration is changed, equilibrium tends to re-establish itself very rapidly. These considerations render it difficult to understand why cropping should cause a general decrease in the concentration of phosphate in the soil solution unless the change is accompanied by substantial increases in the concentrations of those cations (particularly calcium and to a lesser extent magnesium) which tend to form relatively insoluble phosphates; or unless the alkalinity of the soil is increased. It will be observed as between the figures from the cropped and stored soils that calcium and magnesium ions not only do not increase but actually decrease in concentration. On the other hand, from a similar comparison of pH values, there is an increase in alkalinity incidental to cropping in six out of seven cases. In view of the limited number of cases at hand and certain inconsistencies in the data as a whole, it is not clear that increased alkalinities are the only cause of decreased phosphate concentrations.

There are substantial increases in sulfate concentration in cropped and fallowed soils over and above those of stored soils, in all but one case. We observe that the greatest increases are in the fallowed soils, although the cropped soils are not much lower. It is not clear from the present data, whether the increase of this ion is due to oxidation of organic sulfur or to solution of solid-phase sulfate, or both. The significant fact to be noted here is the relative quantitative importance of this ion. In all of our soils which have been depleted in nitrate and chloride content, it is the most abundant ion. The fact suggests itself that in non-alkaline soils, free from excess of chlorides, carbonates and bicarbonates, sulfate is the ion which is mainly responsible for keeping cations in solution when nitrates are diminished. It seems to the writers that this, rather than the usefulness of sulfur as such to the plant, may be the cause of the greatly increased crops frequently obtained by sulfur applications to many soils.

SEASONAL CHANGES IN THE SOIL SOLUTION

In table 4 are presented the analyses of solutions displaced from the seven soils at the beginning and at the end of the ninth growing season, and at the beginning of the tenth season. The data thus cover the critical periods for an

[4] See footnote 3.

entire year. The data from table 4 are recalculated to uniform moisture for each soil in table 5, and the latter is used as the basis for the following discussion.

In considering these data, it must be kept in mind that the soils had all borne crops of barley for 9 consecutive years, while under observation in this laboratory. Many of the soils also had been under intensive cultivation for

TABLE 4

Solutions displaced from cropped (A) soils at beginning and at the end of the growing season (1923) and at the beginning of the next growing season (1924)

SOIL NUMBER	DATE	MOISTURE	pH	PARTS PER MILLION OF DISPLACED SOLUTION							
				NO$_3$	HCO$_3$	SO$_4$	PO$_4$	Ca	Mg	Na	K
		per cent									
7	Apr. 30, 1923	10.7	7.4	174	83	655	1.1	283	106	49	24
	Sept. 4, 1923	12.5	7.6	58	155	432	0.6	193	47	40	9
	Apr. 28, 1924	14.2	7.6	222	142	571	0.6	296	67	52	11
8	Apr. 30, 1923	9.6	7.4	274	93	633	2.5	267	93	31	20
	Sept. 4, 1923	8.4	7.6	88	143	275	1.4	153	56	28	11
	Apr. 28, 1924	13.2	7.2	227	107	441	2.1	232	78	23	10
9	Apr. 30, 1923	11.4	7.6	160	73	·432	0.9	213	75	27	12
	Sept. 4, 1923	13.8	7.8	43	167	121	0.3	107	32	30	7
	Apr. 28, 1924	12.9	7.6	182	98	390	0.5	220	57	28	10
10	Apr. 30, 1923	13.9	7.2	230	40	360	1.2	187	145	23	33
	Sept. 4, 1923	14.4	7.6	40	112	241	0.7	108	38	16	23
	Apr. 28, 1924	16.0	7.2	200	73	423	1.1	216	70	17	25
11	Apr. 30, 1923	12.9	8.2	166	160	645	3.3	213	93	84	39
	Sept. 4, 1923	12.4	7.6	16	234	598	1.2	192	64	44	22
	Apr. 28, 1924	11.4	8.1	286	259	854	2.9	300	102	85	38
12	Apr. 30, 1923	12.1	7.3	115	40	281	2.3	120	46	27	13
	Sept. 4, 1923	13.5	7.6	50	68	184	0.7	80	28	12	9
	Apr. 28, 1924	13.7	7.3	156	49	313	0.7	156	50	18	10
14	Apr. 30, 1923	18.0	8.0	146	107	295	1.3	140	47	56	45
	Sept. 4, 1923	18.7	7.6	13	176	174	0.2	80	23	26	23
	Apr. 28, 1924	18.8	7.6	167	142	380	1.0	168	55	47	49

years before they were assembled for experimental purposes. All soils have now reached a comparatively low yield which varies little from year to year. The average yield of grain in 1923 was about 39 per cent and total dry matter 29 per cent of that obtained in 1915. Under such circumstances, we might legitimately anticipate that whatever changes occur during a given growing season, the condition of the soil at the beginning of each season should be

relatively constant. Such a result is abundantly confirmed by the data presented. Briefly stated, these show that the resultant effect of a crop is to bring about a general diminution of concentration of electrolytes, especially of nitrates, sulfates, and bases in the solutions displaced from the soil, but that there is a tendency toward increased concentrations of such constituents after

TABLE 5

Solutions displaced from cropped (A) soils at the beginning and at the end of the growing season (1923), and at the beginning of the next growing season (1924)

(Results from table 4 calculated to a uniform moisture basis for each soil)

SOIL NUMBER	DATE	MOISTURE	pH	PARTS PER MILLION OF DISPLACED SOLUTION								
				NO_3	HCO_2*	SO_4	PO_4*	Ca	Mg	Na	K	Total
		per cent										
7	Apr. 30, 1923		7.4	149	83	561	1.1	242	91	42	21	1190
	Sept. 4, 1923	12.5	7.6	58	155	432	0.6	193	47	40	9	935
	Apr. 28, 1924		7.6	252	142	649	0.6	336	76	59	12	1527
8	Apr. 30, 1923		7.4	313	93	723	2.5	305	106	35	23	1601
	Sept. 4, 1923	8.4	7.6	88	143	275	1.4	153	56	28	11	755
	Apr. 28, 1924		7.2	357	107	693	2.1	365	123	36	16	1699
9	Apr. 30, 1923		7.6	132	73	357	0.9	176	62	22	10	833
	Sept. 4, 1923	13.8	7.8	43	167	121	0.3	107	32	30	7	507
	Apr. 28, 1924		7.6	170	98	365	0.5	206	53	26	9	928
10	Apr. 30, 1923		7.2	222	40	347	1.2	180	140	22	32	984
	Sept. 4, 1923	14.4	7.6	40	112	247	0.7	108	38	16	23	585
	Apr. 28, 1924		7.2	222	73	470	1.1	240	78	19	28	1131
11	Apr. 30, 1923		8.2	173	160	671	3.3	222	97	87	41	1454
	Sept. 4, 1923	12.4	7.6	16	234	598	1.2	192	64	44	22	1171
	Apr. 28, 1924		8.1	263	259	785	2.9	276	94	78	35	1793
12	Apr. 30, 1923		7.3	103	40	252	2.3	108	41	24	12	582
	Sept. 4, 1923	13.5	7.6	50	68	184	0.7	80	28	12	9	432
	Apr. 28, 1924		7.3	158	49	318	0.7	158	51	18	10	763
14	Apr. 30, 1923		8.0	141	107	284	1.3	135	45	54	43	810
	Sept. 4, 1923	18.7	7.6	13	176	174	0.2	80	23	26	23	515
	Apr. 28, 1924		7.6	168	142	382	1.0	169	55	47	49	1013

* Bicarbonate and phosphate remain as in table 4 (see text.)

the removal of the crop, and by the beginning of the succeeding season these are of the same general magnitude as those of the preceding year in soils which have been continuously cropped. In the light of these results, there can be but little doubt that the reason why a depleted soil continued to give fairly

uniform crops for many years is that it attains an equilibrium which is a function of environmental conditions and the nature of the solid phase. The comparatively small amounts of solutes removed from year to year by the growing plants do not substantially change the composition of the solid phase and hence cannot materially affect the equilibrium.

As stated above, most constituents decrease in concentration in the displaced solutions at the end of the growing season and apparently the losses of dissolved materials incidental to the growing of the crop have not at that time been made good by additions from the solid or gaseous phase. The exception to this generalization is the bicarbonate ion, which is invariably higher at the end than at the beginning of the growing season. The characteristic increase of the partial pressure of CO_2 in the soil atmosphere during the period of ripening of plants as shown by Russell and Appleyard (5) is sufficient to account for the increase of the bicarbonate ion at that stage.

The behavior of phosphate here, as in the cases already considered, is of interest. It seems clear that, whatever the cause, there is a general tendency for phosphate concentrations to diminish during the growing season and to increase during the period between crops. For the most part these fluctuations are consistent with the increases and decreases of alkalinity indicated by the pH values. Here again, however, certain exceptions[5] preclude definite conclusions and it is evident that more highly specialized experiments will be necessary to elucidate all of the vagaries of phosphate behavior.

From both sets of experiments, it seems fair to conclude that in soils which are not subject to the leaching effect of percolating waters, phosphate tends to be reduced in concentration when subjected to conditions incidental to the growing of a crop in spite of the tendency of solid-phase phosphates to dissolve and compensate for the amounts removed by the plant. The generally recognized tendency of many soils to increase in alkalinity during the growing season is probably the most important factor in the decrease of phosphate concentration found at that time. It should, however, be kept clearly in mind that the present data are derived from experiments in which soils were kept in tanks that permitted no escape of drainage water. It is, therefore, still an open question as to how the soil solutions of natural soils with good under-drainage are affected. Soils in which the effects of leaching are to reduce the concentration of calcium and magnesium should tend toward increased (3) concentrations of phosphate in the absence of increases in pH values. With concurrent decreases of alkalinity the effect should be accentuated. This phase of phosphate behavior is now undergoing study in this laboratory.

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[5] Inaccurate determinations of pH values may be the cause of these exceptions due to losses of CO_2 from the displaced solutions during the manipulation. It seems probable that very slight changes in the pH value cause substantial changes in phosphate concentration, so that experimental errors, unless quite small, become significant.

NATURE AND CHANGES OF THE SOIL SOLUTION

The uniformity in behavior with respect to most of the characteristics and changes observed in the displaced solutions from all of the soils studied renders it probable that many of the conclusions arrived at are applicable to soils in general.   Thus the evidence presented may be deemed to be conclusive that, excepting soils which are in a very high state of fertility, fallowing increases the concentration of the displaced solution and presumably also of the soil solution. On the other hand, the effect of cropping is to reduce the concentrations of most constituents in the displaced solution.   When soils have reached a low state of fertility due to continuous cropping the seasonal decrease of concentration to which most of the solutes are subject, is only temporary.   In such soils it may be expected that the initial concentration of the soil solution in any given growing season will be restored to its original magnitude by the beginning of the following season.

In addition to these broad generalizations the nature of the evidence would appear to justify a further statement of a quantitative character as to concentrations and changes of the soil solution in soils consisting largely of mineralized solid-phase constituents.   Soils approaching the extremes of mineralogical composition and those consisting largely of organic detritus are obviously beyond the scope of the present data.   Since we are in the nature of the case dependent upon observations of a limited number of specific individual soils we have first to consider the character of our particular soils with reference to their availability for such generalizations.

The investigations of Hilgard, and of his colleagues and successors, have clearly shown that soils of the arid region in general, not only contain larger totals of the bases used by plants than do the soils of humid regions, but also yield larger amounts of such bases when treated with various solvents.   The evidence afforded by water extractions is particularly cogent and gives indubitable proof of the relatively high degree of solubility of the constituents of typical arid soils.   Observations of freezing-point depressions also show substantially higher total concentrations for soils of arid, as compared with those of humid, regions.   The soils considered in the present paper are from a region of deficient rainfall and, while neither alkaline nor saline in the sense in which these terms are commonly used, are certainly typical of their climatic origin. As such, the total concentrations of their soil solutions are probably higher than those of the average soil from humid regions.   The absolute concentrations of electrolytes in the soil solution inferred from studies of the solutions displaced from our soils, thus probably represent maxima which are not likely to be attained in humid soils, save in exceptional cases.   With this understanding we may venture to suggest certain characteristics of the conventional soil solution based upon the present data.   Referring to table 3, the highest total concentration we have yet observed in a displaced solution was in the stored soil 8, which contained 4093 parts per million at 14.7 per cent moisture.   If

such a soil were reduced to half this moisture content, as might easily happen under cultural conditions in the field, the concentration should approximately double. It seems fair to conclude that the soil solution of soils in general probably seldom exceeds 5000 parts per million at moisture contents corresponding to their optimal water requirements, or 10,000 parts per million at half optimum.

When the concentration of the soil solution is of this order of magnitude it is probably not greatly increased by fallowing and may be diminished thereby. When of lower concentration, and in the generality of cases, the concentration is probably increased by any treatment which stimulates biological activities. With soils having solutions of very low concentrations such treatment may greatly increase the amounts of dissolved matter (cf. 12 S and 12 B). On the other hand, there is but little doubt that cropping a soil continuously even for a limited number of years decreases the concentration of the soil solution in all soils and the greatest rate of loss is probably in those soils which initially had high concentrations (cf. 8S with 8A and 12S with 12A). Soils probably will not prove highly productive when the soil solution at the beginning of the growing season approaches a concentration of 1000 parts per million at optimum moisture content, unless the rate of formation of solutes and particularly of nitrates is especially high during the period covering the early stages of the growth of the crop.

When a soil has been continuously cropped for a number of years it probably seldom contains more than 1500 parts per million of total solutes in its soil solution, and the quantity may be considerably lower than 1000 parts per million at optimum moisture even at the beginning of the growing season. Such soil solutions decrease still further during the growth of the crop and may be reduced to a few hundred parts per million by the end of the period of absorption by the plant, after which they tend to increase and may return to their initial concentrations by the beginning of the next season.

The qualitative characteristics of the soil solution may be made clearer by expressing the results in terms of chemical equivalents. For this purpose we have averaged the data (see table 3) from each set of soils and recomputed these in terms of milli-equivalents. These results are presented in table 6A. It will be observed that the sums of the negative ions are somewhat less than those of the positive ions. The differences are given in the column headed "deficiency." These differences are doubtless due to analytical errors inseparable from determinations based on small quantities of solution. In table 6B we have eliminated the deficiency by proportionate additions to all negative ions.

From table 6B it is evident that the solutions from stored and fallowed soils have the same general qualitative characteristics, consisting largely of nitrates and sulfates, the ratio of nitrate to sulfate being about 3 to 1 in both sets of soils. In the depleted soils this is reversed and the nitrate-sulfate ratio is about 1 to 3. A further change occurs during the growth of crops as shown by the individual soils in table 5 where the nitrate decreases, bicarbonate increases

and sulfate, while usually decreasing, does not ordinarily diminish at so great a rate as does nitrate. The effect upon the proportions of the various anions, however, is minimized here because all of the soils had comparatively low amounts of nitrates at the beginning of the season due to the continuous cropping to which they had been subjected. It is evident that highly fertile soils comparable to most of the "B" or "S" soils, would suffer an extreme reversal of anion composition during the growth of a crop, since the previous work of this laboratory (1) has shown that even such soils lose the greater part of their nitrates after the first few weeks of the growth of barley. The data from the

TABLE 6 A

Average* composition of displaced solutions from cropped (A), fallowed (B) and stored (S) soils after 8 years

SOILS	MOIS-TURE	NEGATIVE IONS MILLI-EQUIVALENTS							POSITIVE IONS MILLI-EQUIVALENTS				TOTAL IONS MILLI-EQUIVA-LENTS
		NO$_3$	HCO$_3$	Cl	SO$_4$	PO$_4$	SiO$_2$	Deficiency	Ca	Mg	Na	K	
	per cent												
A	12.6	2.91	1.44	0.0	9.81	0.06	1.26	4.29	10.14	7.10	1.84	0.68	39.54
B	16.3	25.12	0.87	1.22	8.21	0.06	1.26	6.50	27.88	10.99	2.77	1.61	86.49
S	16.2	16.80	1.20	7.41	4.96	0.17	1.26	2.98	19.02	8.80	5.04	1.92	69.56

* Averages from table 1.

TABLE 6 B

Average* composition of displaced solutions from cropped (A), fallowed (B) and stored (S) soils after 8 years after eliminating deficiency

SOILS	MOISTURE	NEGATIVE IONS MILLI-EQUIVALENTS						POSITIVE IONS MILLI-EQUIVALENTS				TOTAL IONS MILLI-EQUIVA-LENTS
		NO$_3$	HCO$_3$	Cl	SO$_4$	PO$_4$	SiO$_3$	Ca	Mg	Na	K	
	per cent											
A	12.6	3.72	1.84	0.00	12.53	0.08	1.61	10.14	7.10	1.84	0.68	39.54
B	16.3	29.56	1.02	1.44	9.66	0.07	1.48	27.88	10.99	2.77	1.61	86.49
S	16.2	18.37	1.31	8.10	5.43	0.19	1.38	19.02	8.80	5.04	1.92	69.56

* Averages from table 1.

"A" and "S" soils (table 6B) are therefore probably more representative of the qualitative changes in ordinarily fertile soils during the growing season than are those from the seasonal study of the depleted soils. The special interest of the qualitative changes in the soil solution of soils under crop, lies in the fact that the make-up of many nutrient culture solutions has been based upon the imagined composition of the conventional soil solution. We may, therefore, consider what the composition of such a nutrient culture solution should be if it is to simulate the concentration of the soil solution as it exists at any given period. For this purpose we have re-calculated the data from

table 6B in terms of parts per million of the salts which would supply the amounts of solutes shown by the averages of our displaced solutions. These data are presented in table 7.

The combinations of ions, of course, are purely conventional and are based upon the relative solubilities of the various salts. It is not intended to imply that the ions as they exist in the displaced solutions are in these particular combinations or are undissociated. Such a tabulation, however, brings out the extraordinary qualitative differences of composition which must be taken into account when the liquid phase of soils under crop is being considered. Moreover, the results indicate in a more definite manner than we have been able to present heretofore, that a nutrient solution made up in imitation of

TABLE 7

Conventional combinations as salts of ions in displaced solutions from cropped, fallowed and stored soils after 8 years

SALT	CROPPED (12.6 PER CENT WATER)		FALLOWED (16.3 PER CENT WATER)		STORED (16.2 PER CENT WATER)	
	p.p.m.	Proportion	p.p.m.	Proportion	p.p.m.	Proportion
		per cent		*per cent*		*per cent*
NaNO₃...................	156	11.40	235	7.15	428	17.04
KNO₃...................	69	5.04	163	4.96	194	7.72
Mg(NO₃)₂...............	89	6.51	813	24.72	651	25.92
Ca(NO₃)₂..............	—	——	1164	35.39	214	8.52
CaCl₂..................	—	—	80	2.43	450	17.91
MgSO₄.................	354	25.88	—	—	——	—
CaSO₄.................	451	32.97	657	19.98	369	14.69
Ca(HCO₃)₂.............	149	10.90	83	2.52	106	4.22
Ca₃(PO₄)₂.............	8	0.58	7	0.21	20	0.80
CaSiO₃................	92	6.73	87	2.65	80	3.18
Total................	1368	100.00	3289	100.00	2512	100.00
Total Computed to Uniform Water 16.2 per cent	1064		3309		2512	

the probable composition of the soil solution of fertile soils at the beginning of the season is anything but representative of the liquid phase of the soil as it exists at later periods if plants are being grown thereon.

SUMMARY

1. Data are presented covering the composition of the solutions displaced from seven fine sandy loam soils under varied conditions.

2. The conditions represented were those incidental to cropping, fallowing, and maintenance in the air-dry state, all for a period of 8 years.

3. Similar data obtained from the cropped soils at the beginning and at the end of the ninth season and at the beginning of the tenth season of continuous cropping are given.

4. It is concluded that continuous cropping invariably decreases the concentrations of the solutions obtainable from soils by water displacement. On the other hand, fallowing increases the concentrations of such solutions except in the case of soils in a high state of fertility.

5. In soils which have been continuously cropped for some years, the seasonal decrease of concentration of the displaced solution characteristic of soils in general is temporary, and it may be expected that such solutions will increase to their initial concentrations by the beginning of the next season.

6. The characteristic fluctuations in concentration of certain solutes in the displaced solution are discussed. The fluctuations of phosphate concentration are deemed to depend primarily upon the reaction of the soil solution, although the concentrations of certain cations also are involved.

7. Estimates of the quantitative composition of the soil solution of fertile and infertile soils are tentatively suggested.

8. Evidence is presented which tends to show that the qualitative composition of the soil solution in soils under crop is constantly changing. It follows that nutrient culture solutions made up in imitation of the soil solution as it exists at the beginning of the season, cannot represent such solution during the later stages of the growth of crops.

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THE EFFECT ON PRESENT SOIL REACTION OF LONG-CONTINUED APPLICATIONS OF EQUIVALENT AMOUNTS OF HIGH-CALCIUM AND HIGH-MAGNESIUM LIMES[1]

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For more than thirty years the Rhode Island Agricultural Experiment Station has been studying the effects of different forms of lime on plants and soils for the purpose of ascertaining the best and most economical compounds to use, the optimum amounts to apply, and the proper degrees of fineness of the several materials, when present and future availability conditions are considered. While much has been written in past years on the physical, chemical and biological effects of liming soils, little data are extant on the *comparative* effects of periodic, equivalent applications of basic calcium and magnesium compounds on the hydrogen-ion concentrations of cropped field soils over long periods. From the work which has been reported it appears that such applications are thought eventually to produce approximately identical soil-reaction results, the choice of the best material to use being largely an economic matter.

Fifteen years ago the field experiment which furnished the material for this brief paper was begun. Its object was to compare the effects of the continued applications of high-calcium and high-magnesium limes, when used in chemically equivalent quantities (equal neutralizing basis) upon the resulting chemical composition of the soil and also upon plant behavior. The details of the experiment here discussed have been published recently by Hartwell (3) and by Mather (5), the former giving the agronomical data (crop yields), while the latter presents the chemical work performed from time to time upon the soils of the several plats. The reader is referred to these publications for more complete information regarding the history, system of cropping, yields and chemical soil studies. It is sufficient to state here that the same basal fertilizers

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[1] Contribution 309 of the Rhode Island Agricultural Experiment Station.

have been used throughout, and uniform crops have been grown on all the plats. The lime applications per acre have been as follows:

PLAT	KIND OF LIME USED*	1909	1914	1916	1921	TOTAL †
		lbs.	lbs.	lbs.	lbs.	lbs.
74N	High-calcium hydrate................	4,511	2,262	3,096	2,250	12,119
76N	High-magnesium limestone............	6,000	2,820	4,500	2,805	16,125
78N	High-calcium limestone...............	6,000	3,000	4,348	3,435	16,783
80N	High-magnesium hydrate.............	3,750	1,819	2,676	1,830	10,075
82N	None................................	0	0	0	0	0

* Applied on an equal neutralizing basis as determined in the laboratory by standard methods. The limestones were in all cases very finely ground (approximately two-thirds passing a 100-mesh sieve). For the complete analysis of these limes, see reference no. 3 p. 4.

† The equivalent of 9225 pounds of CaO per acre has been applied to each plat.

Prior to the second lime applications, in the spring of 1914, soil samples were taken from each plat and lime-requirement determinations made by the Jones method. The limed plats all showed a requirement of approximately 3,000 pounds of CaO per acre, while the check required 5,000 pounds. Subsequent to this work, no determinations for acidity were made in these soils until 1920, when the author collected a series of samples during the fall and electrometrically determined hydrogen-ion concentrations. During 1921 four more series of samples were taken and similar determinations made.[1] One series of samples also was taken in the early summer of 1922, another in 1923, and two early in 1924. All the data secured appear in table 1.

Before discussing these results, certain "lime-requirement" (calcium absorption) data also will be presented. Exactly 50 gm. of air-dry soil from each of the four samplings taken during 1921 were thoroughly mixed to form a representative sample of each of the five plats for that season, and lime-requirement determinations were made by the Jones modified method (1). Similar determinations also were made on the samples taken in 1924. The results appear in table 2.

The data in tables 1 and 2 indicate that, although added in chemically equivalent quantities, there have been decided differences in the neutralizing powers of the several basic materials employed. This is clearly shown both by the hydrogen-ion concentration determinations and by the lime-requirement tests which indicate the same comparative relationships in all cases. The high-magnesium hydrate has been most efficient as a soil neutralizer, followed by the high-calcium hydrate, the finely ground, high-magnesium limestone and the finely ground, high-calcium limestone in the order named, although there is little difference between the two limestones.

[1] The plats were limed in the autumn after the 1921 soil samples were taken.

By referring to the specific acidities (2, footnote, table 4), as listed in the last column of table 1, it will be seen that the hydrogen-ion concentrations in the soils of the two ground limestone plats are twice as great as in the high-calcium hydrate plat soil, and approximately three times as great as in the high-magnesium hydrate plat soil. The relative standing of these compounds may be explained in part by the differences in the solubilities of the carbonates and bicarbonates resulting from the carbonation of the hydrates in the soil solutions, and in part by the relative surfaces exposed to solution by the vari-

TABLE 1

Hydrogen-ion determinations of field soils treated with equivalent quantities of high-calcium and high-magnesium limes

PLAT	FORM OF LIME	1920 November	1921 May	July	August	September	1922 July	1923 July	1924 April	July	AVERAGE	SPECIFIC ACIDITY
		pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	
74N	High-calcium hydrate...........	7.2	6.6	6.3	6.3	6.3	7.0	6.5	5.8	5.8	6.42	4.0
76N	High-magnesium limestone.......	7.2	6.3	6.1	6.1	6.2	6.0	6.0	5.6	5.7	6.13	8.0
78N	High-calcium limestone.........	6.6	6.4	6.2	6.3	6.4	5.9	5.8	5.6	5.7	6.10	8.0
80N	High-magnesium hydrate.........	7.4	7.1	6.4	6.6	6.7	6.8	6.7	5.9	5.9	6.61	2.5
82N	None.........................	5.2	4.9	4.7	4.9	4.9	4.5	4.5	4.5	4.5	4.73	200.0

TABLE 2

Lime-requirement (Jones method) in pounds per acre on field soils treated with equivalent quantities of high-calcium and high-magnesium limes

Plat..	74N	76N	78N	80N	82N
Treatment............................... }	High-calcium hydrate	High-magnesium limestone	High-calcium limestone	High-magnesium hydrate	No lime
Sampled 1921......................	1,530	1,800	1,530	1,440	3,690
Sampled 1924......................	1,580	2,120	1,670	1,400	4,400
Total crops removed during last 7 years (tons).....................	47.0	48.0	47.0	48.6	29.1

ous-sized particles, for, while the carbonates were both finely ground, the hydrates were impalpable powders of extreme fineness. It hardly seems probable that the time element could be an important factor here. Fifteen years have elapsed since the first lime applications were made, while the last additions were made three years ago. This should have given sufficient time for the attainment of a condition of approximate equilibrium between the soil and the liming materials.

An interesting sidelight on this very point is presented by the yields of several crops, known to be especially sensitive to acid-soil conditions, when grown regularly each year subsequent to an equivalent application of hydrated lime

and ground limestone of different degrees of fineness (4). The crops referred to are alfalfa, beets and barley. During the first three years, the yields were all about the same following initial applications of either hydrated lime or finely ground limestone (80-mesh), but during the next two years the yields were decidedly better where the hydrated product had been used. It thus appears that *finely ground* limestones are less permanent in their effects on acid soils than are the hydrated limes. This is probably largely due to leaching.

It is also of interest that the plat receiving the high-magnesium hydrate has, during the past seven or eight years, produced somewhat larger crops than any of the other limed plats.

From the data here presented, it appears that measurable differences in the ability to neutralize soil acidity are shown between the hydrates and carbonates of high-calcium and high-magnesium limes when applied to field soils in chemically equivalent quantities over long periods of time, and that such differences, to a slight extent, are reflected in crop yields.

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THE RELATION OF MOISTURE AND AVAILABLE NITROGEN TO THE YIELD AND PROTEIN CONTENT OF WHEAT[1]

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A previous investigation (1) showed the effect of available nitrogen in the elaboration of the wheat kernel under both greenhouse and field conditions. The results indicated that the chief factor influencing the yield and protein content of wheat was moisture, when sufficient available nitrogen was present. For the purpose of definitely correlating the effect of different percentages of moisture on the protein content and yield of wheat both with and without an excess of available nitrogen, the following experiment was planned.

Thirty-nine pots were used. Treatments were made in triplicate. Each pot contained the equivalent of 26.5 pounds of oven-dried soil. The soil was obtained from the B_1 plot previously described (1). It is a soil which has been cropped continuously to wheat for 9 years. To the entire series of pots equal amounts of sodium acid phosphate, potassium chloride and lime were added. Palouse Bluestem wheat was planted on May 10, 1923. After a few days' growth the plants were thinned to seven in each pot. An explanation of the various moisture and nitrogen treatments follows.

A number of pots were kept at 25 per cent moisture content. The moisture equivalent[2] was found to be 25, which was assumed to be somewhere near the optimum moisture content; others were kept at 20 and 15 per cent throughout the entire life cycle of the wheat plant. The moisture content of all pots was kept at these different percentages by carefully weighing the pots and adding the required amount of water at frequent intervals. A series was included in which the moisture content of the soil was kept at 25 per cent until the fruiting period, then reduced to 15 per cent for the remainder of the growth and ripening period of the wheat plant. Another series was included which was treated just the reverse; that is, the moisture of the soil was kept at 15 per cent until the beginning of the fruiting period, then raised to 25 per cent for the fruiting and ripening period. To all of these series nitrogen was added in two different systems of treatments; one, the entire amount added at the time of planting; the other, fractional amounts added cumulatively, or at five different intervals in the life cycle of the wheat plant until the total quantity added equalled the entire addition made at the time of planting. An excess of nitrogen was desired, hence nitrogen at the rate of 200 pounds per acre in the form of sodium nitrate was added in both methods of applications. Check series of the soils also were included which did not receive nitrate additions but which had the moisture percentages varied.

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[1] Published with permission of the Director of the Idaho Experiment Station.

[2] Determined by Prof. G. R. McDole, Soil Technologist of the Idaho State Experiment Station.

The results given in table 1 plainly show the effect of the three different moisture percentages on the plants grown without nitrate fertilizer. At a moisture content of 25 per cent, the yield and the weight of 100 kernels were greater, while the protein content was lower than at 20 or 15 per cent. Changes of moisture are noted directly in the yield of wheat and weight per 100 kernels. The shriveled condition of the kernels from pots 19–21 and 28–30 partly accounts for the increased protein content of wheat.

TABLE 1

Yield and protein content of wheat as affected by different treatments of moisture and available nitrogen

POT NUMBER	NaNO₃ ADDED PER ACRE PER TREATMENT	MOISTURE	NUMBER OF HEADS	TOTAL YIELD OF WHEAT	TOTAL YIELD OF STRAW	RATIO OF GRAIN TO STRAW	WEIGHT OF 100 KERNELS	PROTEIN CONTENT
	lbs.	per cent		gm.	gm.		gm.	per cent
4–6	None	25	8	4.57	8.5	1–1.86	3.21	16.82
19–21	None	20	7	2.83	7.0	1–2.47	2.52	17.48
28–30	None	15	7	2.97	6.3	1–2.12	2.83	18.01
Sodium nitrate added May 10, date of planting								
1–3	200	25	20	13.63	27.6	1–2.03	3.35	17.44
16–18	200	20	18	10.47	20.4	1–1.91	3.49	17.91
25–27	200	15	16	9.80	16.4	1–1.68	3.28	18.30
Sodium nitrate added May 10, June 4, June 29, July 24, and August 18								
7–9	40	25	19	14.40	25.9	1–1.80	3.57	17.67
22–24	40	20	20	12.23	21.8	1–1.78	3.47	18.97
31–33	40	15	16	9.40	17.0	1–1.81	3.17	19.77
Soil moisture changed at beginning of fruiting period; nitrate added May 10								
13–15	200	25 to 15	21	11.00	25.9	1–2.35	3.51	19.35
37–39	200	15 to 25	22	13.07	25.4	1–1.94	3.02	17.06
Soil moisture changed at beginning of fruiting period; nitrate added May 10, June 4, June 29, July 24, and August 18								
10–12	40	25 to 15	20	12.83	23.8	1–1.85	3.57	19.55
34–36	40	15 to 25	19	12.90	24.4	1–1.89	3.18	17.76

When the additions of nitrogen were made at the time of planting, the effect of the three different moisture percentages on yield was in favor of the higher moisture content. This series has the largest number of heads, the greatest yield of both wheat and straw, and the lowest protein content. The results for the other two series, 20 and 15 per cent, follow in decreasing order for number of heads, yield of wheat and straw, and in increasing order for the protein content. In all three series, plump wheat kernels were produced. The kernels in the 15 per cent series weighed only slightly less than the others.

When the series receiving the entire addition of nitrate at the time of planting are compared with their respective check soils, the effect of available nitrogen on the yield and protein content is shown to be very marked. The effect of cumulative additions of an equivalent amount of nitrate, made at five stages during the growth of the wheat plant, to soils kept at varying moisture percentages, (25, 20, and 15 per cent) was consistent with the data just discussed. The yields of wheat and straw follow in order of the moisture content, the 25 per cent moisture content showing the heaviest yields. The weight per 100 kernels also is found to be in the same order. The greater amount of protein, however, is found in the 15 per cent moisture series, and it decreases in the remaining two moisture series in reverse order of the yield and the weight per 100 kernels. Here again is seen the effect of moisture, on the yield and protein content of wheat even in the presence of an excess of available nitrogen; also the effect of available nitrogen in increasing the protein content of wheat over that of wheat grown on the check soils without nitrate additions, for all three moisture series.

In part 3 of table 1 are given the data on the effect of adding the entire nitrate additions at the time of planting to soils which are kept at 25 and 15 per cent moisture until the beginning of the fruiting period when the moisture content in one series was lowered to 15 per cent and in the other, raised to 25 per cent. This was done to note the effect of a high and low moisture plane, at different periods of growth of the wheat plant, on the yield and protein content of wheat.

The series at 25 per cent moisture content up to the fruiting period and 15 per cent thereafter, yielded slightly less of both grain and straw than the series at 25 per cent moisture content during the entire life cycle of the plant, but the protein content was higher. The former series corresponded more nearly to actual growing conditions in this section. In this first series, however the yield of grain is increased and the weight of 100 kernels and the percentage of protein both decreased in comparison with the series to which only 15 per cent moisture was added up to the fruiting period and then increased to 25 per cent for the ripening period of the wheat plant. This series developed an unnatural condition which would seldom occur under field conditions; that is, when the moisture was increased to 25 per cent at the beginning of the fruiting period, the plants immediately began to throw out new shoots and these developed and matured very slowly. When the plants were harvested, a considerable number of immature, shriveled heads were present. This is shown in the lower weight of 100 kernels and the lower protein content. Under field conditions, the results would have been similar with excessive moisture during the fruiting period.

Practically the same conclusions can be drawn from the results given in part 4 of table 1. The treatments differ from those in part 3 only in one particular; that is, the nitrate treatments were made in five cumulative applications rather than the entire amounts at the time of planting. Here again wheat grown on

pots receiving 25 per cent moisture for the entire period gave a larger yield and contained less protein than that from soil with a moisture content of 25 per cent reduced to 15 per cent.

Pots 37–39, and 34–36 showed similar yields to pots 13–15 and 10–12, the protein content and weight per 100 kernels were considerably lower, for the same reason as stated above.

A comparison of the effect of varying amounts of moisture, on wheat grown with nitrate added in entirety at the time of planting, and in five cumulative additions, is more easily seen when table 1 is studied.

The effect of moisture on the wheat plant is easily compared on the check soil, without nitrate additions. In part 2, the two systems of nitrate additions are compared at the three different moisture contents. Here it is seen that for the series of soils kept at 25 per cent moisture, nitrate added in five cumulative additions produces wheat which is slightly higher in yield, weight per 100 kernels, and protein content than when all the nitrate is added at once at the time of planting. The yield and protein content also are higher with the cumulative additions for the 20 per cent series, with an approximately equal yield and a higher protein content in the 15 per cent series, the respective series to which all the nitrate was added at the time of planting. These differences are small, as would be expected, because of the initial large addition of available nitrogen. Under average field conditions much wider variations might be expected because the available nitrogen is not present in such large quantities in the soil.

Changing the moisture content at the fruiting period from optimum to low, results in a lower yield, but a higher protein content than when the optimum moisture is continued throughout the entire life cycle of the plant. In this same experiment, the higher protein content and yield are found in the wheat grown on soils receiving the cumulative additions, rather than all the nitrate at once. However, both treatments yield wheat of large kernels and high protein content.

When the moisture content is reversed, that is the soil maintained at 15 per cent until the fruiting period, then raised to 25 per cent, a lower yield occurs than when the soil is kept at the optimum moisture content of 25 per cent. Comparing the above moisture content with the reverse treatment, that is, 25 per cent up to the fruiting period, then reduced to 15 per cent, only a slight difference is noted in the total yield, while a difference of approximately 2 per cent in the protein content is noted in favor of the low over the high moisture content during the ripening period. Changing low to high at fruiting time causes more shoots to grow, resulting in an immature wheat kernel. While the yield may be slightly greater, the kernels are smaller and the quality of wheat poorer. This particular result would scarcely be realized under field conditions, because the immature heads would never ripen in sufficient time to affect the yield.

By way of summary it may be concluded from the results given here and elsewhere (1) that in the presence of an abundance of available nitrogen,

moisture plays an important rôle in the yield and protein content of wheat. When the available nitrogen is sufficient, as in this experiment, for a maximum growth of the plant, both yield and protein will be influenced, but yield more than protein.

It makes little difference, under optimum moisture conditions, whether the 200 pounds of nitrate is added at the time of planting or throughout the life cycle of the plant, provided sufficient is applied at planting time to insure the presence of a liberal quantity in the soil during the fruiting and ripening period.

TABLE 2

Effect of variations in rainfall on wheat yields under field conditions

	1914	1917		1922		1923	
	Acre yield	Acre yield	Protein content	Acre yield	Protein content	Acre yield	Protein content
	bu.	bu.	per cent	bu.	per cent.	bu.	per cent
B₂ continuous................	38.6	5.7	12.29	11.1	14.44	38.8	10.43
D₈ wheat....................	38.2	10.07	12.14	11.8	13.19	43.0	13.26
E₁₀ plots...................	30.7	8.20	13.17	16.6	13.45	42.2	10.21
Average...................	35.82	7.99	12.53	13.17	13.67	41.3	11.30

Monthly rainfall

	1914	1917	1922	1923
	inches	inches	inches	inches
January.......................	3.58	2.86	2.04	3.93
February......................	1.95	1.76	1.49	1.71
March.........................	0.76	1.13	2.50	1.56
April..........................	1.76	3.63	1.47	2.52
May...........................	2.00	1.81	0.47	1.44
June..........................	1.36	0.72	0.22	3.37
July...........................	0.70	0.05	0.00	1.19
August........................	0.00	0.00	1.52	0.26

Fall, 1916—Not heavy precipitation; slightly below normal.
Fall, 1921—Normal, fairly heavy.
Fall, 1922—Slightly below normal.

Cutting down the moisture content during the fruiting period results in a smaller yield, but a considerable increase in protein content over the optimum moisture series. This condition is more nearly similar to actual field conditions.

The greatest effect of a lack of moisture on the check soil, which is low in available nitrogen, is shown on the yield. With an optimum moisture content, a greater yield is obtained than when less moisture is present. Favorable moisture conditions allow more plant-food to become available and result no doubt in better nutrition of the plant.

An example of the effect of moisture on the yield and protein content of wheat grown under field conditions is clearly shown by a comparison of a few

years' data from a rotation experiment now under way on the Agricultural Experiment Station Farm. This experiment includes three plots that have grown wheat continuously since 1914. Each year the yield of wheat and the proteins content have been determined. Government records of rainfall also have been kept. The data on rainfall, yields and protein content of wheat for the years, 1914, 1917, 1922 and 1923 are given in table 2. The protein content of the initial wheat crop grown in 1914 was not determined.

The effect of seasonal rainfall on the yield of wheat is very clearly shown when the average yields for the four years and rainfall are compared. Since the plots have been producing wheat each year since 1914, the fertility is much lower than if a rotation or fallow were practiced. In 1917 and 1922 the yields were much lower than in the first year, 7.99 bushels in 1917,[3] 13.17 bushels in 1922, and 35.82 bushels in 1914. The rainfall for the years 1917 and 1922 was below normal, especially during May, June and July. The yield for 1923, however, a very rainy year, averaged 41.3 bushels, an abundant yield in spite of the fact that these particular plots had raised ten continuous crops of wheat. The favorable distribution of moisture no doubt accounts in a large measure for these large differences, favoring bacterial activities and causing more plant food to become available.

We find that the wheat grown in 1917 and 1922 had a higher protein content than that grown in 1923. On soil low in available nitrogen, when the yield is small because of a low rainfall, the protein content is increased over that of wheat grown on the same soil with an abundance of moisture. Also the protein content is raised because of a partially shriveled condition of the wheat kernel whenever sufficient moisture is lacking during the fruiting and ripening period.

In 1923, however, with favorable moisture conditions and a high yield, the protein content was only 11.3 per cent. On a soil low in fertility, even in the presence of abundant moisture, a high yield of wheat results in a low protein content.

It is noted that the wheat plant carefully regulates the protein content, and if there is a lack of available nitrogen or moisture, yield is the first to be decreased. With both moisture and available nitrogen present in abundance throughout the life cycle of the plant, yield will be affected the greater, with protein showing an increased percentage over wheat grown on a soil low in available nitrogen. In soil poor in available nitrogen, a low moisture content also may result in a low yield, but an increase in the protein content of the kernels due to a shriveling of the grain caused by a moisture deficiency during the fruiting and ripening period.

The results of this work fully corroborate conclusions previously drawn (1).

[3] Considerable winter killing took place in this crop.

SUMMARY

1. A high moisture content in a soil containing sufficient available nitrogen for the maximum growth and development of the wheat plant, results in high-yielding wheat containing a high percentage of protein.

2. A low moisture content in the soil containing an excess of available nitrogen results in a lower yield of wheat but a higher protein content.   A part of the higher protein content may be due to a shriveling of the wheat kernel.

3. A high or optimum moisture content in a soil, which has considerable nitrogen available for the wheat plant in the early periods of growth, but an insufficient amount during the fruiting and ripening periods for maximum growth, results in a high yield of wheat of low protein content.

4. A low moisture content in a soil which has sufficient nitrogen available to the wheat plant during the early stages of growth, but an insufficient amount for the fruiting and ripening periods, results in a low yield of wheat, the percentage of protein varying according to the degree to which the wheat is shriveled from moisture deficiency.

5. Under field conditions a high moisture content, such as sometimes occurs during seasons of abundant rainfall, properly distributed during the growing period, on average soil will produce a high yielding wheat with a low protein content.   A highly fertile soil under the same conditions also produces a high yield of wheat but may show an increase in protein content if sufficient available nitrogen is present during the entire life cycle of the plant.   If the protein is not increased, the effect of the increased fertility of the soil will usually be reflected in a higher yield of wheat.   A soil cropped continuously to wheat will produce more in a season of abundant rainfall than in a dry season, especially if rains are lacking during the fruiting and ripening periods.   High yields and good quality of wheat require proper moisture conditions and a fertile soil.

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FURTHER STUDIES ON SOIL PROFILES[1]

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It was shown in a former contribution (2) that the soils of Michigan may be logically placed into two groups designated simply as northern and southern. Reference was made also to a transitional group. Further mention of these groups may be found in another publication (1). Furthermore, the desirability of studying soil profiles was emphasized. If samples of soil are taken to arbitrary depths for laboratory studies or field investigations, erroneous results may be obtained. That is to say, the roots of the plants may, and doubtless do, come into contact with horizons that vary markedly in their nature; and if two or more of these horizons are mixed in sampling, the true environmental conditions of the plant-root system may not be brought to light. It may be cited, for example, that the third or brown horizon of the northern profile may exhibit very different properties if portions of the second or fourth horizon are mixed with it in the sampling.

In order to bring out differences that may occur chiefly with the colloidality of the various horizons in several profiles, additional investigations have been conducted. The heat-of-wetting method appeared to be valuable in bringing out some of these differences. These studies were made in the usual way, with the use of water, nitrobenzole, 95 per cent alcohol and absolute alcohol. The results are summarized in table 1.

In comparison with this work on the mineral soil profile some similar work was done on muck profiles, the results of which are given in table 2. Inasmuch as the ash content of the various horizons of organic deposits varies considerably and has such a tremendous influence on the other properties, the ash content of these horizons also was determined.

The data in table 1 show strikingly the difference in activity of the humus horizon on being treated with the different liquids used. It has been observed that the heat of wetting of organic soils with water is many times greater than that of mineral soils. The data here recorded show the heat of wetting of the humus horizon with water to be much greater than that of the other horizons. This is not true of the other liquids used, with the possible exception of 95 per cent alcohol.

[1] Published by permission of the Director of the Experiment Station.

TABLE 1
Heat produced per 50 gm. of soil with different liquids

SOIL TYPE	HORIZON	WATER	NITRO-BENZOLE	95 PER CENT ALCOHOL	ABSOLUTE ALCOHOL
		calories	calories	calories	calories

Soils of southern group

SOIL TYPE	HORIZON	WATER	NITRO-BENZOLE	95 PER CENT ALCOHOL	ABSOLUTE ALCOHOL
Coloma (Southern)	1. Virgin numus soil................	109.32	34.88	67.23	32.30
	2. Yellow concentrated horizon......	49.96	27.74	29.73	16.39
	3. Basal soil, sandy................	20.53	22.17	22.28	14.26
	4. Parent material, sand............	17.29	12.43	7.41	5.69
Bellefontaine	1. Virgin mold and humus, 0 to 3 inches.........................	179.42	52.06	111.96	
	2. Pale yellowish sand, leached......	65.52	54.33	56.00	38.02
	3. Reddish horizon, concentrated....	121.94	90.89	129.00	113.93
	4. Basal layer.....................	123.91	96.36	127.20	106.52
Waukesha	1. Dark brown humus soil, 0 to 10 inches.........................	153.64	48.32	112.50	32.45
	2. Yellowish loam..................	113.05	55.90	90.56	66.17
	3. Reddish yellow tight clay........	135.36	93.81	142.75	122.92
	4. Basal soil, gravelly.............	40.71	45.09	42.24	32.11
Napanee	1. Humus soil.....................	235.38	48.67	147.80	38.47
	2. Pale, yellowish gray silt.........	105.81	60.15	86.09	59.08
	3. Brownish mottled upper portion horizon of clay concentration...	114.83	93.67	109.22	93.56
	4. Lower portion of clay concentration........................	142.98	116.60	146.10	109.10
	5. Parent till clay.................	104.46	89.11	97.10	96.87

Soils of northern and transitional group

SOIL TYPE	HORIZON	WATER	NITRO-BENZOLE	95 PER CENT ALCOHOL	ABSOLUTE ALCOHOL
Coloma (transitional)	1. Virgin forest soil................	79.28	34.61	44.70	14.28
	2. Gray leached sand...............	21.62	15.21	11.86	5.69
	3. Yellow concentrated layer........	34.40	31.18	28.23	18.25
	4. Basal soil, sand.................	28.03	27.70	22.27	14.24
	5. Substratum, sand...............	11.43	13.12	11.11	5.58
Emmet	2. Gray leached sand...............	12.73	12.44	12.61	4.26
	3. Brown horizon, loamy sand.......	63.97	37.54	44.71	19.28
	4. Basal soil, sand 20 to 36 inches...	21.62	16.60	11.86	10.67
	5. Substratum sand................	13.98	14.50	10.38	3.55
Mancelona	Virgin forest soil 0 to 30 inches...	227.10	36.24	104.40	
	Gray leached sand...............	43.41	27.74	28.26	7.27
	Brown loamy sand...............	48.55	41.65	37.21	21.69
	Basal soil loamy sand............	39.55	36.67	31.99	
	Gravelly parent material.........	52.31	39.48	44.63	27.17

Note: The specific heats of the liquids were taken as follows:

Water.. 1.00
Nitrobenzole... 0.35
Absolute alcohol... 0.56
95 per cent alcohol...................................... 0.58

In the case of some of these profiles the heat of wetting of the humus horizon with nitrobenzole and absolute alcohol is slightly greater than that of the other horizons but in a few cases it is actually lower. There is not very much difference between the heat of wetting of the mineral, or lower, horizons with the different liquids. In the case of the heavier types of soil the heat of wetting of the lower horizons with nitrobenzole and absolute alcohol is remarkably high. The reddish brown horizon or the one of greatest concentration of colloids, either mineral or organic, shows considerably greater activity with all liquids used than do the coarser-textured horizons adjacent to it.

TABLE 2

Heat produced per 25 gm. of muck with different liquids

NAME	HORIZON	ASH	WATER	NITRO-BENZOLE	ABSOLUTE ALCOHOL
		per cent	*calories*	*calories*	*calories*
Shaw's Muck	0 to 6 inches well decomposed.......	31.46	638.15	34.27	16.34
	6 to 12 inches slightly coarser, lower ash.............................	17.95	724.10	28.99	11.51
	12 to 18 inches finely divided........	10.12	690.30	28.25	18.84
	44 to 48 inches colloidal...........	64.91	295.95	33.26	56.36
Farm Lane	0 to 6 inches well decomposed.......	28.91	669.25	28.30	22.08
	6 to 12 inches slightly coarser.......	23.57	752.00	33.44	20.33
	24 to 36 inches somewhat fibrous....	7.31	638.75	31.80	61.82
	48 to 60 inches colloidal............	28.77	488.95	28.88	15.27

These differences are significant in that in a given soil profile there are horizons that react quite differently to a given liquid, and also to different liquids when brought into contact with them. Of course, when heat is evolved it must be concluded that either chemical or physical reaction, or both, have taken place. It is an expression of energy change. Thus, when horizon 1 is relatively inert to nitrobenzole or absolute alchohol and horizon 3 or 4 reacts very differently it seems logical to conlude that the nature of the colloids is strikingly different too—that is, if we assume that the colloids are responsible largely for the heat-of-wetting results. It would appear that when a given substance is used in studying colloids, for example, by absorption or heat of wetting, important differences may not be brought out. Yet it seems that the heat-of-wetting method has great possibilities in the determination of the colloidality of soils.

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ACTION OF STABLE MANURE IN THE DECOMPOSITION OF CELLULOSE IN TILLED SOIL[1]

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INTRODUCTION

It is well known that stable manure exercises a favorable influence on the decomposition of cellulose in tilled soil. A. Koch (8) tried in 1890 to demonstrate this quantitatively, but the method used was very primitive and could never be expected to gain anything like general application in work of this kind. It was only after Charpentier (5) in 1920 had worked out in this laboratory a reliable method for the quantitative estimation of cellulose in soil, that the factors affecting the decomposition of cellulose in soil also could be accurately investigated.

In 1921 Charpentier (6) published some investigations dealing with the effect of stable manure on the decomposition of cellulose in different kinds of soils of different reaction and moisture content. Stable manure was invariably observed to have a distinctly favorable effect on the decomposition of cellulose, in soils having the optimum moisture content for the action of microörganisms. The reaction has hardly any influence in this connection, for according to Charpentier's experiments, a vigorous decomposition of cellulose can take place in acid as well as alkaline soils, the addition of lime having no effect. This is of course due to the fact that the cellulose-fermenting organisms which occur plentifully in all soils, belong to widely different groups, including aerobic and anaerobic bacteria of different kinds, as well as actinomycetes and moulds. According to the reaction of the soil and its other properties, one or the other of these groups of organisms will become predominant in the decomposition of the cellulose.

As to the mode of activity of manure in this connection, there are really only two possibilities to be considered: first, the cellulose decomposing organisms in the manure may cause a more vigorous decomposition of the cellulose occurring in the soil, or, second, it may be that the nutrient substances in the

manure bring about a more vigorous development of the microörganisms already present in the soil, including the cellulose splitters, thus promoting cellulose decomposition. This would amount to an indirect biological action due to the manure. Finally, a combined direct and indirect biological action might also be imagined.

Up to this time the first of these theories undoubtedly has had the most supporters. It is almost a dogma that one of the most valuable properties of stable manure is its large content of microörganisms which upon being added to the soil greatly stimulate the microbiological changes taking place. However, we may search in vain in the available literature for a really convincing proof of the direct microbial action of manure. On the other hand, several circumstances speak *against* any such action when some of the most important factors are carefully considered from a bacteriological point of view.

We are now of the opinion that the addition of cultures of certain microörganisms or mixtures thereof to the soil has no real or lasting effect on it. It appears that a certain equilibrium between the different species is established in the soil, an equilibrium which is not disturbed by an occasional inoculation with one kind of organism or another. In order to alter the microbial life of the soil it is necessary to effect changes of a different nature which will modify its physical or chemical properties, e.g., draining, working, liming or manuring. By such means the microflora may be stimulated as a whole, or certain groups of organisms may be stimulated, the result often being an increase in the fertility of the soil in question. Thus *a priori* it is not very likely that an inoculation of the soil with the microörganisms introduced with the manure can exercise a direct influence on the biological condition of the soil itself. The bulk of the microörganisms present in manure, are specifically intestinal bacteria, and we have no certain knowledge as to the ability of these organisms to develop in the soil. It is true that livestock manure contains, for example, powerful cellulose-splitting organisms, but such organisms can always be found also in the soil. Very probably the bulk of the microörganisms introduced into arable soil with stable manure die there after a short time instead of increasing the microflora. It must be remembered that the conditions in the soil differ very widely from those in the intestines, for example, with regard to temperature and aeration.

Again, if the influence of stable manure is attributed chiefly to its content of nutrient substances readily assimilable by the microörganisms already present in the soil, then it is suggested that the determining factor is the nitrogen content of the manure, especially the ammoniacal nitrogen.

Charpentier (6) carried out a short investigation comparing the effect of 2 per cent of cow manure containing 0.16 per cent of ammonia nitrogen with that of an equivalent amount of ammonium sulfate as regards ammonia nitrogen. The pots contained 1 per cent of cellulose in the form of finely cut filter paper. Two parallel pots of each kind were prepared.

The results showed the effects of the cow manure and the ammonium sulfate, respectively, to be the same, which again favors the view that the ammonia nitrogen in the manure is the deciding factor under the circumstances

TABLE 1

Influence of various ammonium salts upon cellulose decomposition in the soil

POT NUMBER	AMMONIUM SALTS ADDED PER KILOGRAM OF SOIL		2 MONTHS		4 MONTHS		6 MONTHS		8 MONTHS	
			Cellulose	Average	Cellulose	Average	Cellulose	Average	Cellulose	Average
		mgm. NH_4-N	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Ia	None	—	0.71	0.70	0.66	0.59	0.62	0.57	0.47	0.39
Ib			0.69		0.53		0.52		0.31	
IIa	$(NH_4)_2SO_4$	10.2	0.56	0.58	0.51	0.50	0.40	0.36	0.30	0.29
IIb			0.59		0.48		0.32		0.28	
IIIa	$(NH_4)_2SO_4$	20.4	0.47	0.45	0.39	0.44	0.36	0.33	0.29	0.26
IIIb			0.43		0.49		0.30		0.22	
IVa	$(NH_4)_2SO_4$	40.8	0.29	0.27	0.15	0.18	0.13	0.14	0.06	0.07
IVb			0.26		0.21		0.16		0.09	
Va	NH_4NaHPO_4	24.1	0.36	0.36	0.30	0.25	0.24	0.21	0.18	0.17
Vb			0.35		0.19		0.19		0.16	
VIa	NH_4NO_3	10.2	0.45	0.45	0.34	0.31	0.24	0.26	0.19	0.18
VIb			0.44		0.27		0.27		0.18	
VIIa	NH_4NO_3	20.4	0.27	0.27	0.18	0.21	0.16	0.17	0.10	0.11
VIIb			0.27		0.24		0.17		0.12	
VIIIa	CH_3COONH_4	20.4	0.49	0.48	0.44	0.38	0.34	0.32	0.30	0.27
VIIIb			0.46		0.32		0.30		0.24	
IXa	$(NH_4)_2CO_3$	20.4	0.40	0.46	0.25	0.32	0.21	0.27	0.13	0.21
IXb	$+2NH_4HCO_3$		0.52		0.39		0.32		0.30	

in question. This isolated trial, of course, is insufficient for the drawing of any definite conclusions.

NEW INVESTIGATIONS

If the reason for the favorable action of the stable manure on the course of the cellulose decomposition is primarily to be sought in its content of ammonia

nitrogen, then the action should naturally be the same in whatever form this material might be added to the soil, provided of course that the amounts of ammonia nitrogen in the soil samples to be compared with respect to cellulose decomposition were always the same.

In the first place, a series of experiments was instituted in which different ammonium compounds were added to the same soil (a heavy clay soil of neutral reaction from the Central Agricultural Experiment Station) to which 1 per cent of finely cut filter paper was added (Munktell's No. 10). The soil with cellulose was divided among a number of pots each holding 1 kgm. of soil, after which 20.4 mgm. of ammonia nitrogen was added to each pot in the form of different ammonium salts. This addition corresponds to the amount of ammonia nitrogen added with 1 per cent of manure containing 0.2 per cent of ammonia nitrogen. The ammonium salts used in this investigation were ammonium sulfate $((NH_4)_2SO_4)$, acid sodium ammonium phosphate $(NH_4NaHPO_4+4H_2O)$, ammonium nitrate (NH_4NO_3), ammonium acetate (CH_3COONH_4), and ammonium carbonate $((NH_4)_2CO_3+2NH_4HCO_3)$.

The pots were closed with paraffined corks in the middle of which short glass tubes packed full of cotton wool were inserted. By this means the evaporation of water is reduced to a minimum while a certain amount of ventilation is obtained. The water lost by evaporation from the pots was not replaced during the experiments without the solids and cellulose being estimated in the soil. The cellulose was then recalculated with respect to soil of the original water content.

For the sake of control, quantities of the different ammonium salts corresponding to double and half the above-mentioned amount of ammonia nitrogen (20.4 mgm. per kgm. of soil) also were taken. The cellulose content of the soil in the different pots was estimated at intervals of two months during a period of 8 months, the pots being kept at room temperature.

METHOD OF ANALYSIS

The cellulose was estimated by Charpentier's method (5) with some modifications.

After the contents of the pot had been mixed, 20 gm. was weighed out in a 150-cc. Lovén flask , and the sample was set to dry for 24 hours in a thermostat at 42°C. The water was thus reduced to about 1 per cent. Then 100 cc. of Schweitzer's reagent was added by means of a Berglöf pipette with a Geissler-Miescher stopcock. By drying the sample, the dilution of the Schweitzer's reagent by the water of the soil is avoided; it is important that the reagent should have the right strength.[2]

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[2] The reagent is conveniently made as follows:

To a solution of 500 gm. of crystallized copper sulfate in 25 liters of water in a large glass cylinder is added 275 cc. of ammonia of sp. gr. 0.91, with stirring, at a temperature of about 40°C. The precipitated copper hydroxide will be coarse, quickly sinking to the bottom; the supernatant salt solution is siphoned off, the precipitate is mixed with water to the original volume, and after settling, the clear liquor is siphoned again. This washing is repeated two or three times after which the precipitate is freed from the water as far as possible, transferred to a glass stoppered 12-liter flask, and dissolved in 8 liters of ammonia, sp. gr. 0.91, being shaken at intervals during 2 to 3 days, to saturation. The reagent thus prepared contains about 1.5 gm. of copper per 100 cc.

After the stopper of the Lovén flask had been fastened by a clamp (fig. 1), which was designed by E. Sandberg, the flask was fixed in a shaking machine capable of holding 10 flasks and making 60 revolutions per minute, the length of the flask being at right angles to the axis of the machine. After shaking for one hour they were allowed to stand overnight. About 60 cc. of the clear liquor was carefully decanted into a dry Lovén flask which was then closed with a rubber stopper having two holes, one for a 50-cc. pipette reaching to the bottom of the flask and the other for a short glass tube which was connected with a hand pump. The solution was slowly pumped up until the level stood somewhat over the mark, whereupon the pipette was closed, and the rubber stopper removed. Exactly 50 cc. was measured

Fig. 1. Lovén Flask with Special Stopper Used in the Experiments

off into a 300 to 400-cc. beaker, and the cellulose was precipitated by the addition of 200 cc. of 80 per cent ethyl alcohol while stirring with a glass rod. As the subsequent filtration is more rapid when the precipitate has completely settled, this operation was postponed until the following morning. According to Barthel's suggestion, the Gooch crucible recommended by Charpentier was replaced by a 35-cc. alundum crucible (of medium fine porosity) of which the wall was glazed about two-thirds of the way down from the rim. This crucible was fixed to a suction flask as usual by means of a rubber connection and a funnel tube. The solution was carefully transferred to the crucible so that the bulk of the cellulose precipitate remained in the beaker. By means of two rinsings with 35 cc. and 25 cc. of 12 per cent hydrochloric acid, respectively, the greater portion of the precipitate was removed to the crucible, whereupon the remaining particles of cellulose were detached from the beaker by means of a glass

rod tipped with a rubber tube, and transferred by means of 35 cc. of cold distilled water from a wash bottle. In these successive transferences and the subsequent washings, care was of course taken that the crucible was sucked empty after each addition. In order to get rid of a quantity of humic acids which are also dissolved in Schweitzer's reagent and later precipitated by the alcohol the crucible was filled with 2 per cent caustic potash solution. As a rule the filtrate here was first colored brown by humates, later on becoming colorless. The washing was then continued with 35 cc. of 2 per cent hydrochloric acid (as it is easier to wash a precipitate free from salt or acid than from alkali) and was concluded with 35 cc. of cold distilled water. To facilitate the drying, the cellulose was treated (without previously emptying the pump flask) with 25 cc. of 95 per cent alcohol and 25 cc. of ether in due turn. The crucible was then allowed to stand for one hour at 100°C. in a water oven, and then in a desiccator to cool. The cellulose was now in the form of a snow white shell-like film which could easily be loosened from the crucible. With the help of a little silver spoon it was transferred to a recently ignited and cooled platinum crucible, and ignited after weighing, the loss in weight being determined on cooling. The difference between the two weighings gives the amount of the cellulose in 10 gm. of the soil mixture; the percentage is obtained by multiplying by 10. In cases where the greatest accuracy is desired, account may be taken of the amount of water remaining after the drying of the soil sample in the thermostat; this residual water must be estimated in a parallel test.

In our preliminary trials the cellulose was dried in the alundum crucible to constant weight, after which the incineration was carried out direct, i.e., without transferring the cellulose to a platinum crucible. This procedure always gave high results because of the retention of more or less water by the porous material under the glaze. On igniting the crucible this residual water, of course, was lost, thus causing the error in question.

As the cellulose is extracted from the soil in the way described above, the incineration of the washed and dried cellulose precipitate cannot be avoided. Of the extract obtained by treating the soil with Schweitzer's reagent, 50 cc. was used without previous filtration, and it therefore sometimes happened that minute particles of soil were present therein; this, however, does not affect the result if the precipitate is incinerated. In addition, the cellulose absorbs iron compounds, but not aluminum compounds, at least for the soil with which we are concerned. There is no objection to filtering the soil extract through asbestos or glass wool, but as this was not necessary, as was shown by the control analyses, it was naturally omitted.

The advantage of the alundum crucible over the Gooch crucible in work of this kind is evident; even if the latter is prepared with the greatest care, there is always the risk that particles of asbestos may become detached on account of the unavoidable changes in pressure, so that channels are formed through which a portion of the cellulose escapes. In working with an alundum crucible this error of course is avoided. Further, the Gooch crucible as a rule must be repacked, while the alundum crucible is always ready for the next analysis. To begin with, ordinary unglazed alundum crucibles were tried, but they soon proved unsuitable as the copper chloride could not be completely washed out. It was only when they had been glazed as described above that the difficulty was overcome. It nearly always happens that some copper salt creeps up

into the porous wall under the glaze, but with our present modification of the method, this does not influence the results.

The above described method of working can be applied only to mineral soils; when dealing with humus soils, the sample for analysis must be submitted to a further preparation consisting, according to Charpentier's directions, of the admixture of 10 per cent of unslaked lime. In this way the humus substances are fixed; otherwise they will prevent the solution of the cellulose in Schweitzer's reagent. The lime is carefully incorporated in the sample by grinding in a mortar after which the mixture is transferred to a beaker and dried at about 40°C. After drying, the mixture is ground once more, transferred back to the beaker, moistened with water and dried. The procedure is then as already described, except that the sample after shaking with the Schweitzer's reagent must stand for 2 to 3 days before the sedimentation is complete.

Turning to the results of the first series of experiments, the figures in table 1 show the influence of the different ammonium salts with equivalent amounts of ammonia nitrogen to be practically the same. Absolute agreement could hardly be expected in fermentation experiments of this kind. In pots V, a and b, 24.1 mgm. of ammonia nitrogen were added by mistake instead of 20.4 mgm.; hence the discrepancies in the cellulose figures for these pots. It is particularly interesting to note that in the pots containing *ammonium nitrate*, the effect was approximately double that observed in the pots containing the same amounts of ammonia nitrogen in the form of other salts. On the other hand, in the pots with half the amount of ammonium nitrate, (10.2 mgm. ammonia nitrogen) the amount of cellulose decomposed was about the same as in the other pots which contained 20.4 mgm. of ammonia nitrogen. This difference is obviously due to the simple fact that in ammonium nitrate there are two nitrogen atoms, one in each radical, and that both of these are equally available to the cellulose-decomposing organisms. The significance of nitrate nitrogen in cellulose fermentation was pointed out in 1904 by van Iterson (7).

Two further series of experiments were carried out on the lines just described, in which we restricted the number of different ammonium salts but included in each case a mixture of cow and horse manure, the amount of ammonium salt added being calculated on the basis of the content of ammonia nitrogen in the manure. Both series in other respects were quite identical with one another.

In order that the manure used be quite homogeneous, about 1 kgm. of 3 to 4 months' old manure was chopped to pieces, mixed with a small spade and put through a mincing machine. After another chopping up and mixing, it was again passed through the machine and mixed once more. From the resulting product, the different portions were directly weighed off for the cellulose pots, and also for the estimation of nitrogen and water.

In such investigations as are described below, one must of course have some guarantee that the method of analysis used for the estimation of ammonia in the manure really gives as accurate results as possible. If all the nitrogen

present in the manure as ammonia is not obtained in the method employed, e.g., if some of it is bound to the manure by adsorption, or, on the other hand, if nitrogen originating from higher nitrogenous compounds is split off as ammonia during the course of the analysis, the values obtained for ammonia nitrogen in the manure will naturally be wrong. Again, as the amounts of ammonia nitrogen added in the form of various ammonium salts must be regulated according to the ammonia nitrogen found in the manure by analysis, it is obvious that the method of analysis employed here must be perfectly reliable if really equivalent conditions are to be attained through the different additions. We have therefore subjected the methods available for the estimation of ammonia nitrogen in manure to a special examination.

In these estimations, made simultaneously, the methods of Boussingault and of Baragiola and Schuppli were compared. According to the former, 50

TABLE 2

Comparison of methods of Boussingault and of Baragiola and Schuppli

AMMONIA NITROGEN ADDED PER 50 GM. OF MANURE	AMMONIA NITROGEN			
	Boussingault method		Baragiola and Schuppli method	
	Recovered	Difference	Recovered	Difference
mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
0.00	90.09	—	75.04	—
0.00	85.82	—	75.11	—
25.06	114.87	−1.85	99.89	0.25
25.06	113.75	−0.73	103.46	−3.32

gm. of the manure was treated with MgO and about 500 cc. of water; 1 cc. of paraffin oil also was added to prevent frothing. The mixture was boiled at ordinary pressure, and the liberated ammonia absorbed by 0.1 N H_2SO_4. The distillate collected amounted to about 300 cc. In Baragiola and Schupplis' method, also carried out on 50 gm. of manure, MgO and about 100 cc. of distilled water were added, and the mixture was distilled to dryness at a pressure of 15 mm. of mercury, at 35°C., the distillate being received in 0.1 N H_2SO_4. After the addition of some fragments of pumice, the entire distillate was boiled for several minutes to eliminate carbon dioxide, and titrated on cooling with 0.1 N NaOH and methyl red. Both methods were controlled thus: To 50 gm. of the same manure was added 25 cc. of ammonium sulfate solution of known strength, and this mixture was then analyzed for ammonia. The mixture was first allowed to stand for 1 hour with occasional shaking in order to get the adsorption equilibrium established. This investigation is set forth in table 2. The percentage loss is calculated on the $(NH_4)_2SO_4$ nitrogen.

The parallel estimations, on the whole, show good agreement. For the manure alone, Baragiola and Schuppli's method gave about 15 per cent less

ammonia than Boussingault's. Both methods accounted quantitatively for the nitrogen added with the ammonium sulfate, which shows that no adsorption took place. It is thus impossible to decide on the basis of these figures which method is the right one to use, though the balance of probability is in favour of the vacuum method which offers milder conditions to the higher nitrogen compounds of the manure.

When the experiments were started it became necessary to make a choice, and we decided on the more convenient method of Boussingault. The *ammonia nitrogen figures for manure in tables 5 and 6, are based on Boussingault's method.* At the same time, the ammonia nitrogen in the manure was in both these cases also estimated by Baragiola and Schuppli's method, so that the results could be checked if necessary.

The scheme of the experiments was as follows:

Pots I, a and b: 1000 gm. soil plus 10 gm. filter paper, plus 30 cc. water,

Pots II a and b: 1000 gm. soil, plus 10 gm. filter paper, plus 10 gm. manure (16 mg. ammonia nitrogen) , plus 22.5 cc. water.

Pots III, a and b: 1000 gm. soil, plus 10 gm. filter paper, plus 20 gm. manure (32 mgm. ammonia nitrogen), plus 15 cc. water.

Pots IV, a and b: 1000 gm. soil, plus 10 gm. filter paper, plus 40 gm. manure (64 mgm. ammonia nitrogen).

Pots V, a and b: 1000 gm. soil, plus 10 gm. filter paper, plus 30 cc. $(NH_4)_2SO_4$ solution (= 32 mgm. ammonia nitrogen).

Pots VI, a and b: 1000 gm. soil, plus 10 gm. filter paper, plus 3.9 cc. NH_4NO_3 solution (= 16 mgm. ammonia nitrogen) plus 26 cc. water.

Pots VII, a and b: 1000 gm. soil, plus 10 gm. filter paper, plus 7.7 cc. NH_4NO_3 solution (= 32 mgm. ammonia nitrogen) plus 22.3 cc. water.

Pots VIII, a and b: 1000 gm. soil, plus 28 cc. water.

The water content of the manure and filter paper was estimated at about 80 per cent and 6 per cent, respectively, and the addition of water to the various pots was regulated accordingly. That is, the water content was the same in all the pots as in no. IV, a and b, or between 18 and 19 per cent, which for mineral soils of the type used in our experiments (clay soil) is the optimum for bacteriological metabolism experiments.

Two analyses of the filter papers used (Munktell no. 10) gave the following results:

	WATER	ASH	CELLULOSE (BY DIFFERENCE)
	per cent	*per cent*	*per cent*
A	5.73	0.42	93.85
B	5.87	0.64	93.49

From these figures, the amount of cellulose added was calculated at 0.90 per cent.

At the same time, a series of direct determinations of cellulose also were made on the filter paper by Charpentier's method. The amounts of finely cut filter

paper given in table 3 were placed in Lovén flasks, and the Schweitzer's reagent added directly. The calculated amounts given in the table are obtained by the multiplication of the weight (in grams) of the filter paper used, by 0.9349; for the difference between the weight of the sample of the same filter paper and the water plus ash, had previously given the figure 93.49 per cent of cellulose. The values found by direct estimation thus agree fairly well with those obtained by difference.

TABLE 3

Direct determinations of cellulose in filter paper

SAMPLE NUMBER	FILTER-PAPER TAKEN	CELLULOSE		DIFFERENCE	CELLULOSE FOUND
		Calculated	Found		
	gm.	*gm.*	*gm.*	*gm.*	*per cent*
1	0.2098	0.1961	0.1944˙	0.0017	92.66
2	0.2099	0.1962	0.1990	−0.0028	94.81
3	0.1029	0.0962	0.0968	−0.0006	94.07
4	0.1030	0.0963	0.1004	−0.0041	97.48
5	0.0301	0.0281	0.0284	−0.0003	94.35
6	0.0301	0.0281	0.0304	−0.0023	101.00

As part of the cellulose might be retained in the soil by adsorption, and thus escape estimation, some further investigations were made in this connection. Into each Lovén flask was placed 20 gm. of soil, previously dried at 42°C., which contained 2.26 per cent of water. The amounts of cellulose given in

TABLE 4

Adsorption of cellulose by soi l

SAMPLE NUMBER	CELLULOSE ADDED		CELLULOSE FOUND		CELLULOSE LOSS ACCORDING TO B	
	Filter paper	Cellulose in filter paper	A	B		
	gm.	*gm.*	*gm.*	*gm.*	*per cent*	*mgm.*
1	0.2104	0.1967	0.1914	0.1923	2.24	4.4
2	0.2106	0.1969	0.1928	0.1937	1.63	3.2
3	0.0975	0.0912	0.0834	0.0838	8.11	7.4
4	0.0995	0.0930	0.0874	0.0878	5.59	5.2
5	0.0329	0.0308	0.0252	0.0253	17.86	5.5
6	0.0304	0.0284	0.0242	0.0243	14.44	4.1

table 4 also were added. The corresponding amounts of pure cellulose are calculated according to the foregoing analyses. The Schweitzer's reagent was added immediately, after which the estimations were made as usual. The cellulose figures given under A were obtained by multiplying the analytical figures by 2, while under B, the water in the soil was taken into consideration.

On an average, 5.0 mgm. of cellulose out of 20 gm. was adsorbed by the soil in question (table 4). In the cellulose estimations in the two last series, corrections were made both for the residual water in the soil after drying, and

for the cellulose adsorbed by the soil. The results of these two series, both carried out according to the same scheme, as given in tables 5 and 6, must therefore be regarded as representing the highest degree of accuracy obtainable by the technique which we employed. Pots VIII, a and b, are not included in tables, as these blank tests always gave negative results with respect to cellulose content. The parallel pots generally show as good mutual agreement in

TABLE 5

Cellulose decomposition in soil—corrections made for residual water in soil

POT NUMBER	ADDITIONS PER KILOGRAM OF SOIL		IMMEDIATELY		2 MONTHS		4 MONTHS	
			Cellu-lose	Aver-age	Cellu-lose	Aver-age	Cellu-lose	Aver-age
		$\frac{mgm.}{NH_4\text{-}N}$	per cent	per cent	per cent	per cent	per cent	per cent
Ia			0.78		0.52		0.51	
	None			0.87		0.53		0.48
Ib			0.95		0.53		0.44	
IIa			0.82		0.49		0.33	
	10 gm. manure	16		0.80		0.51		0.31
IIb			0.78		0.52		0.29	
IIIa			0.78		0.40		0.23	
	20 gm. manure	32		0.85		0.38		0.24
IIIb			0.92		0.36		0.26	
IVa			0.78		0.26		0.20	
	40 gm. manure	64		0.80		0.27		0.18
IVb			0.83		0.28		0.15	
Va			0.80		0.37		0.28	
	$(NH_4)_2SO_4$	32		0.85		0.35		0.26
Vb			0.88		0.34		0.23	
VIa			0.78		0.34		0.26	
	NH_4NO_3	16		0.83		0.34		0.27
VIb			0.89		0.34		0.28	
VIIa			0.79		0.23		0.11	
	NH_4NO_3	32		0.81		0.22		0.13
VIIb			0.82		0.21		0.16	

cellulose content as could reasonably be expected. It is quite remarkable that the initial values found differ so greatly from those calculated (about 0.90 per cent of cellulose), the average error amounting to about 8 per cent. As the initial values almost without exception are too low, the error must lie in the technique. Since the method of analysis itself is characterized by great accuracy, as shown by tables 3 and 4, it is obvious that the sampling or the mixing of the soil and cellulose must be at fault. To settle this question, we made the experiments reported below.

Into 1 kgm. of the same soil as was used in all the experiments, was mixed 10 gm. of filter paper which had been passed twice through a meat-mincing machine. The cellulose thus obtained was much like meal and could easily be mixed with the soil so as to produce an apparently homogeneous mixture. From this, five samples of 20 gm. each were taken for the estimation of cellulose, while a sample of unmixed soil was taken for a blank test. As the soil

TABLE 6

Cellulose decomposition in soil—corrections made for cellulose adsorbed by the soil

POT NUMBER	ADDITIONS PER KILOGRAM OF SOIL		IMMEDIATELY		2 MONTHS		4 MONTHS	
			Cellulose	Average	Cellulose	Average	Cellulose	Average
		$\frac{mgm.}{NH_4-N}$	per cent	per cent	per cent	per cent	per cent	per cent
Ia	None		0.83	0.79	0.45	0.42	0.48	0.45
Ib			0.75		0.39		0.41	
IIa	10 gm. manure	17.5	0.75	0.80	0.41	0.41	0.33	0.33
IIb			0.85		0.42		0.33	
IIIa	20 gm. manure	35.0	0.82	0.88	0.34	0.36	0.25	0.25
IIIb			0.93		0.38		0.25	
IVa	40 gm. manure	70.0	0.79	0.83	0.21	0.24	0.17	0.18
IVb			0.87		0.27		0.18	
Va	$(NH_4)_2SO_4$	35	0.78	0.78	0.26	0.28	0.23	0.23
Vb			0.78		0.30		0.23	
VIa	NH_4NO_3	17.5	0.83	0.88	0.32	0.32	0.24	0.24
VIb			0.93		0.32		0.24	
VIIa	NH_4NO_3	35	0.70	0.75	0.15	0.15	0.12	0.11
VIIb			0.79		0.15		0.11	

was used just after drying at 42°C., and thus contained only 1.15 per cent of water, the Schweitzer's reagent was added direct, the cellulose being estimated as usual. The results are given in table 7, corrected for moisture in the soil as well as for adsorption.

The investigation shows that when using ground filter paper, the cellulose figures obtained are very near the theoretical values. The cut fragments of filter paper, about 2 by 2 mm. in size, as used before, cannot be mixed with

the particles of soil to the same degree as the cellulose meal. It follows that in weighingout the sample, some of the bits of filter paper became separated from the mixture and remained behind. Having cleared up this point, we changed over to ground filter paper in the cellulose fermentation experiments now in progress. Even if the initial values, and therefore the other cellulose figures given in tables 5 and 6, are subject to a relative error of about 8 per cent, this does not hinder the interpretation of the results.

It may be said that these results confirm in a very striking manner the theory that the ammonia nitrogen in the manure is the cause of the favorable influence of the latter on cellulose fermentation in soil. The amounts of cellulose found after a certain time in the pots containing equivalent amounts of ammonia nitrogen agree with one another, while on the other hand, the halved and doubled amounts of ammonia nitrogen give correspondingly higher and

TABLE 7

Cellulose determinations on ground filter paper mixed with soil

SAMPLE NUMBER	CELLULOSE	
	Calculated	Found
	per cent	*per cent*
1	0.925	0.927
2	0.925	0.880
3	0.925	0.846
4	0.925	0.945
5	0.925	0.865
Blank	0.000	0.000
Mean value		0.893±0.019

lower figures, respectively, for the undecomposed cellulose found in the soil. Still closer agreement is obtained if the values for the ammonia nitrogen added with the manure are calculated from the results obtained by Baragiola and Schuppli's method. In this way we found 15, 30 and 60 mgm. of ammonia nitrogen for the manure pots in table 5, and 16, 32 and 64 mgm. for those in table 6. As we already pointed out, it is probable that the above method gives more accurate results, for in Boussingault's method the possibility of some of the higher nitrogenous compounds of the manure breaking down into ammonia is by no means excluded. If, therefore, the additions of ammonium salts are calculated, as we have done, on the basis of the results obtained by Boussingault's method for determining the content of ammonia nitrogen in manure, then the quantities of salts added will probably be too large. This again in effect will make the cellulose fermentation in the manure pots appear to be somewhat less vigorous, by comparison, than should be the case.

The ability of ammonium nitrate, to act as a "double" source of nitrogen as referred to above, is clearly expressed by the experiments set forth in tables 5 and 6, indicating the amount of ammonium nitrate equivalent to the stable

manure and ammonium sulfate in respect to ammonia nitrogen. It is seen that the ammonium nitrate is twice as effective as the manure and the ammonium sulfate, while in amount corresponding to half the equivalent of ammonia nitrogen its effect is exactly the same as that of the two other additions in question.

The results of these experiments may have a wider general significance than appears from the special investigations reported. In the Bacteriological Department of the Central Agricultural Experiment Station, a long series of experiments (2, 3 and 4) have been in progress for a number of years to elucidate the progress of the nitrification of stable manure in soil. These have shown that it is chiefly the ammonia nitrogen of the soil which is nitrified, while as a rule, by no means all of the available ammonia nitrogen is utilized. Now it is shown by the above investigations that the ammonia nitrogen of manure also affects the decomposition of cellulose in tilled soil in such a way that the amount of decomposition after a certain lapse of time stands in direct proportion to the amount of ammonia nitrogen added with the manure. These later investigations therefore confirm the former ones, and permit us to formulate the general rule that the effect of the nitrogen of stable manure during the first year of growth on the microbial metabolism in tilled soil may most probably be ascribed to the ammonia nitrogen of the manure. The remaining nitrogen in the manure consists for the most part of proteins from the epithelial cells of the intestinal tract and from microörganisms, that are being mineralized only very slowly.

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After the foregoing was written we have made some further experiments in order to determine definitely whether the microörganisms added with the stable manure are of any decided importance for the fermentation of cellulose in the soil. The experiments described above have shown that most probably only the ammonia nitrogen added with the manure is the cause for the favorable influence.

1. The same clay soil used in our earlier experiments was thoroughly mixed with finely ground filter paper (1 per cent) and then divided into two parts. The one portion was supplied with 2.3 per cent of stable manure, previously sterilized in an autoclave at 120°C. for 2 hours. The second part was supplied with 2 per cent of unsterilized manure. The ammonia content of the unsterilized manure was 0.163 per cent and of the sterilized manure 0.142 per cent. Both soil mixtures were put into 200 cc. bottles and stopped with paraffined corks provided with a short glass tube packed with cotton. Two bottles of each kind were prepared and then stored at room temperature. After two months the cellulose was determined in the usual manner and the following average values were obtained:

per cent of cellulose

Unsterilized soil plus sterilized manure.....................................0.63
Unsterilized soil plus unsterilized manure................................0.57

2. The same soil was sterilized in an autoclave at 120°C. for 2 hours and then supplied with 1 per cent of ground filter paper. Then the mixture was transferred to 200 cc. bottles and sterilized in the autoclave at 105°C. for 15 minutes. This short sterilization at a rather low temperature was thought to be sufficient, the spores in the soil already having been killed by the first sterilization. On the other hand, the paper could not be mixed into the soil before the first sterilization as the cellulose tends to be decomposed at higher temperatures. The bottles were stopped with rubber stoppers provided with glass tubes packed with cotton. The stoppers were previously sterilized in alcohol and the glass tubes in a dry oven. Two of these bottles were inoculated with 2.3 per cent of sterilized manure and 1 per cent of unsterilized soil, two with 2 per cent of unsterilized manure and 1 per cent of unsterilized soil and two, finally, with 2 per cent of unsterilized manure only. These bottles were stored at room temperature together with the bottles mentioned above, and analyzed after two months for cellulose. The following averages were found:

per cent of cellulose

Sterilized soil plus 2.3 per cent sterilized manure plus 1 per cent sterilized soil...0.13
Sterilized soil plus 2 per cent unsterilized manure plus 1 per cent unsterilized soil.0.14
Sterilized soil plus 2 per cent unsterilized manure.........................0.16

It appears unmistakable from both these experiments that the cellulose fermenters added with the manure do not cause the favorable influence of the manure upon the cellulose fermentation in the soil. This effect appears to

be due to the ammonia nitrogen added with the manure. As seen from the figures above, sterilized manure has just the same effect as unsterilized manure when, as in this case, the amounts of ammonia nitrogen are equivalent.

That the cellulose fermentation takes place so much more rapidly in case of sterilized soil merely may be attributed to the increase of the amount of ammonia nitrogen which enters during the sterilizatipn by the splitting off of ammonia from higher nitrogen compounds. By analysis there were found 56.0 mgm. of ammonia nitrogen per kilogram of the sterilized soil, while the unsterilized soil was practically free from ammonia.

Experiments which are now being made in this laboratory by J. Arlington Anderson, indicate that this amount of ammonia nitrogen, 56.0 mgm. per kilogram of soil, which was split off by sterilization, is quite sufficient to establish the rapid cellulose fermentation found above.

SUMMARY

1. The method for determination of cellulose in soil, originally worked out by Charpentier in our laboratory, has been further modified and perfected by us. In its present form this method affords a valuable contribution to the technique of metabolism experiments in soil biology. It is possible to determine the power of the organisms present in various soils to decompose cellulose, and the influence of various factors on this process; just as the nitrifying power, nitrogen assimilation, carbonic acid formation, etc., are determined.

2. The favourable influence of stable manure upon cellulose fermentation in the soil, which was found by Charpentier is due to the nitrogen present in the manure which is available to microörganisms. Microörganisms added with the manure are of no practical importance in normal soils since sterilized manure acts in the same manner as unsterilized manure. The ammonia nitrogen in the manure can be exchanged by other ammonia compounds with the same result.

3. The cellulose fermentation in autoclaved soil, inoculated either with manure or unsterilized soil, proceeds much more rapidly than in unsterilized soil because of the ammonia nitrogen split off from higher nitrogen compounds during sterilization.

RESIDUAL EFFECTS OF FORTY YEARS CONTINUOUS MANURIAL TREATMENTS. I. EFFECT OF LIME ON DECOMPOSITION OF SOIL ORGANIC MATTER

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The origin of the idea of greater destruction of soil organic matter by caustic lime than by lime carbonates may be traced to early studies made by Hess (5) on certain plots of the "General Fertilizer Series" located at this station. The interpretation by Hopkins (6) of these data gave prominence to this work and led to a wide acceptance of his teachings on this important subject resulting in an unjust discrimination against the use of lime other than neutral carbonates. Frear (3, p. 151) under whose direction the studies of Hess were conducted made the following statements concerning the far reaching results of Hopkins' conclusions:

> This experiment and the conditions have been thus fully presented and discussed, because the references of 1899–1900 were made the basis for conclusions much farther reaching than any the writer ventured to make; and these, in turn, have constituted the grounds for an extensive commercial exploiting of the merits of ground limestone as contrasted with the old-fashioned burnt lime applications, which are declared to burn up the humus, whereas the carbonate is said to conserve it.

Since the studies of Hess in 1899–1900, the same plots have been thrice sampled and studied in a similar manner, in 1911 by MacIntire (9) and 1915 and 1921 by the authors of this paper. Each succeeding study where the soil of the *four tiers* was composited into one sample, representative of each treatment, gave results quite similar to the earlier studies. The soil treated with limestone in every instance contained more organic matter and nitrogen than that treated with burned lime. However, when the plots of each tier were separately studied, as was done in case of the 1921 samples, the data secured threw a new light on this much mooted question and leads to conclusions entirely contrary to those cited above. The primary purpose of this paper is, therefore, to present this new evidence supported by more detailed studies concerning the comparative effects of these two forms of lime on the decay of soil organic matter at the end of forty years of continuous treatment during which time the soils have received total applications equivalent to 80,000 pounds per acre of lime carbonate and 40,000 pounds of burned lime respectively. The data secured as the result of the earlier studies where the four tiers are composited as a unit will be presented together with the 1921 figures

computed to the same basis. These figures will afford an opportunity of studying to a limited extent the progressive changes in organic carbon and total nitrogen content of these soils as the result of the two lime treatments in comparison with the untreated soil.

PENNSYLVANIA FIELD PLOT EXPERIMENTS

The detailed plan and scope of these old field experiments have been published in several reports dealing with the yields of the various treatments (4) and will be described here only in relation to the particular plots under consideration. In the scheme of treatments are included studies of the comparative values of burned lime[1] and pulverized limestone, applied without further manurial treatment, on plots numbered 23 and 34, respectively. A 4-year rotation had been followed consisting of corn, oats, wheat and hay (mixed clover and timothy). Two tons of burned lime have been applied to each corn crop and 2 tons of limestone to both the corn and wheat ground. From

TABLE 1

Summary of the results secured on the 1899, 1911, 1915, and 1921 (samples of the four tiers composited)

PLOT NUMBER	SOIL TREATMENT	ORGANIC CARBON				NITROGEN			
		1899	1911[*]	1915	1921	1899	1911	1915	1921
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1, 14, 24, 36	Untreated............	1.64	1.4821	1.5385	1.4277	0.1244	0.1122	0.1150	0.1110
23	Burned lime..........	1.47	1.4661	1.5227	1.4509	0.1172	0.1199	0.1145	0.1155
34	Limestone............	1.67	1.6929	1.7971	1.7355	0.1341	0.1222	0.1205	0.1252

[*] The 1911 studies include only one check plot (no. 24).

1881 to 1921, therefore, the corn ground has received a total of 20 tons of burned lime as compared to 40 tons of limestone for corn and wheat. Reference to the diagram will show that four tiers are included in the experiment; thus each of the four crops are grown every year. Five untreated plots are shown on the diagram, only four of which are included in the chemical studies.[2]

A review of the above figures shows that in each case the limestone treated soil contains more organic carbon and nitrogen. The later studies apparently serve to substantiate the work of Hess.

Conclusions by Hess, 1899

From the above, the destructive effects of lime in the caustic condition, upon the humus is clearly shown. The amount of nitrogen is decreased by a continued use of caustic lime without the additions of other manures.

[1] From 1881 to 1910 the burned lime was slaked in piles before spreading. Since 1910 raw ground lime (CaO) has been used.

[2] Plot 8 has always given abnormal yields and for this reason is excluded from the composite samples of untreated plots.

Conclusions by Frear 1899

The action of caustic lime to decrease the humus of the soil (C $\times$ 1.724) is very distinctly shown in these results from field trials. The annual loss, compared with that of the unfertilized plot is 0.21 ton in excess, equivalent to the quantity in one ton of stable manure. The deficiency of nitrogen on the limed plots corresponds with the results of laboratory trials, but the relative gain of nitrogen on the land treated with ground limestone is unexpected and merits further and more detailed study. In the absence of data as to the composition of the soil at the time when the fertilizer experiment began, it is impossible to discover whether there has been an absolute loss or gain of humus in any case (2).

Treatment	Treatment	Treatment	Treatment
Untreated	Untreated	Untreated	Untreated
30 N+P+K	30 N+P+K	30 N+P+K	30 N+P+K
2 T. CaCO3	2 T. CaCO3	2 T. CaCO3	2 T. CaCO3
Ca SO4	Ca SO4	Ca SO4	Ca SO4
72 N+P+K	72 N+P+K	72 N+P+K	72 N+P+K
48 N+P+K	48 N+P+K	48 N+P+K	48 N+P+K
24 N+P+K	24 N+P+K	24 N+P+K	24 N+P+K
P+K	P+K	P+K	P+K
72 N+P+K	72 N+P+K	72 N+P+K	72 N+P+K
48 N+P+K	48 N+P+K	48 N+P+K	48 N+P+K
24 N+P+K	24 N+P+K	24 N+P+K	24 N+P+K
P+K	P+K	P+K	P+K
Untreated	Untreated	Untreated	Untreated
2 T. CaO	2 T. CaO	2 T. CaO	2 T. CaO
2 T.CaO+6 T.Manure	2 T.CaO+6 T.Manure	2 T.CaO+6 T.Manure	2 T.CaO+6 T.Manure
72 N+P+K	72 N+P+K	72 N+P+K	72 N+P+K
10 T. Manure	10 T. Manure	10 T. Manure	10 T. Manure
48 N+P+K	48 N+P+K	48 N+P+K	48 N+P+K
8 T. Manure	8 T. Manure	8 T. Manure	8 T. Manure
24 N+P+K	24 N+P+K	24 N+P+K	24 N+P+K
6 T. Manure	6 T. Manure	6 T. Manure	6 T. Manure
P+K	P+K	P+K	P+K
Untreated	Untreated	Untreated	Untreated
Ca SO4	Ca SO4	Ca SO4	Ca SO4
30 N+P+K	30 N+P+K	30 N+P+K	30 N+P+K
72 N+P+K	72 N+P+K	72 N+P+K	72 N+P+K
48 N+P+K	48 N+P+K	48 N+P+K	48 N+P+K
24 N+P+K	24 N+P+K	24 N+P+K	24 N+P+K
Untreated	Untreated	Untreated	Untreated
P+K	P+K	P+K	P+K
24 N+K	24 N+K	24 N+K	24 N+K
24 N+P	24 N+P	24 N+P	24 N+P
K	K	K	K
P	P	P	P
N	N	N	N
Untreated	Untreated	Untreated	Untreated

FIG. 1. PLAN OF PENNSYLVANIA FIELD PLOT EXPERIMENTS "GENERAL FERTILIZER SERIES" 1881–1921

Nitrogen applied as dried blood on plots 2, 12, 35, 9, 10, 11, 17, 19 and 21.
Nitrogen applied as nitrate of soda on plots 26, 27, 28 and as sulfate of ammonia on plots 30, 31 and 32.

Conclusions by Hopkins based on the figures of Hess

The data, as stated by Hopkins, indicate that the effect of caustic lime as compared with ground limestone was equivalent to the destruction of 37½ tons of farm manure in 16 years, or more than two tons per year to the acre (6); also that there is a liberation of more than $7.00 worth of nitrogen for every

ton of burned lime used during the 16 years. In a like manner the difference of 0.2 per cent of organic carbon between the two limed plots was computed to the equivalent of 37.6 tons of fresh manure.

It is of interest to note that in computing the difference of 0.0169 per cent nitrogen to the equivalent of pounds per acre Hopkins used as his weight per acre 9 inches of soil 2,224,800 pounds as suggested by Hess. However, the carbon figures were computed on the basis of 2,700,000 pounds per acre 9 inches. Hopkins thus gets an actual difference of organic matter greater than reported by Hess. (Hess computes a difference of 3.9 tons of humus (C × 1.724) in favor of limestone and Hopkins 4.7 tons).

The far-reaching effect of these computations is well known to those familiar with the "Illinois System of Permanent Agriculture." Burned lime has been eliminated in the middle west largely as the result of these figures, while in the east Hopkins' conclusions concerning lime have apparently not had so great an effect. Although the work of Hess is based on experiments conducted at this station no reference to his findings has ever been made in publications at the Pennsylvania Station in an attempt to show the superiority of one form of lime over another. As the result of this more conservative stand, eighty-five producers of the various forms of agricultural lime are offering their products for sale in this state.

The 1899 and 1911 results have been fully discussed by Frear (3, p. 141–148) and need no further comment here. A comparison of the 1899 and 1915 results indicates that during the sixteen years between these two periods the untreated soil lost 188 pounds of nitrogen; that treated with burned lime, 54 pounds; and the soil treated with limestone, 272 pounds. The untreated soil in 1899 contained 144 pounds of nitrogen in excess of the burned lime soil while in 1915 the difference is only 10 pounds and in 1921 the untreated soil contains 90 pounds less than the burned lime soil. If the organic carbon is computed to the equivalent of pounds of organic matter per acre 2,000,000 pounds it will be seen that in 1899 the untreated soil contained 5861 pounds organic matter in excess of the burned lime soil as compared to a difference of 906 pounds in 1915. In 1921 the untreated soil contained 800 pounds less than found on the limed soil. The untreated soil is therefore decreasing in both nitrogen and organic matter at a greater rate than the lime treated soil. The following summary shows the increase (+) or decrease (−) of nitrogen and organic matter on the limed soils above that found on the untreated soil, expressed in pounds per acre at the end of 18, 36, and 40 year periods.

TREATMENT	ITEM	AFTER 18 YEARS	AFTER 36 YEARS	AFTER 40 YEARS
		pounds	*pounds*	*pounds*
Burned lime	Gain or loss of nitrogen	−144	−10	+90
Burned lime	Gain or loss of organic matter	−5,861	−546	+800
Limestone	Gain of nitrogen	+194	+110	+284
Limestone	Gain of organic matter	+1,035	+8,915	+10,713

Note: The 1911 figures are omitted due to the fact that only one untreated plot was included.

The apparent superiority of the limestone treatment is brought out in this summary. There is a marked increase in organic matter and nitrogen greatly in excess of that shown by the burned lime soil. This unusual condition which gave rise to the teachings concerning the superiority of limestone is due, as will be shown later to the presence of a *charcoal deposit* on the limestone plot of tier 4, the significance of which will be discussed in the succeeding pages.

Table 2 shows the average annual yields for the first forty years of the experiment. It will be noted that up to the sixth rotation with the exception of the first, the untreated soil has outyielded the burned lime plot, after that period the untreated soils fall behind. The soil treated with limestone, however,

TABLE 2

Yield of the four crops based on the average pounds of dry matter produced in each of the ten rotations 1881–1921

TREATMENT	AVERAGE ANNUAL YIELDS OF DRY MATTER PER ROTATION ON 4 ACRES										
	1882–1885	1886–1889	1890–1893	1894–1897	1898–1901	1902–1905	1906–1909	1910–1913	1914–1917	1918–1921	1882–1921
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
Untreated (Plots 1,8, 14, 24, 36)	14,153	14,784	14,474	11,567	8,685	10,119	8,969	9,073	8,559	7,909	10,829
Burned lime.....	14,467	13,438	12,930	10,597	7,733	11,389	9,392	12,236	11,293	10,867	11,434
Limestone..	15,701	14,807	14,751	12,909	9,748	11,817	10,301	11,589	11,372	10,905	12,390

TABLE 3

Relative yields based on the first rotation of the untreated soil taken as 100

	ROTATIONS										AVER-AGE
	1	2	3	4	5	6	7	8	9	10	
Untreated soil................	100	104	102	81	61	71	63	64	60	56	77
Burned lime..................	102	95	91	75	55	80	66	87	79	77	81
Limestone...................	119	105	104	91	69	83	73	82	80	77	88

has outyielded the untreated plots throughout the ten rotations. A comparison of the yields of the two limed plots shows that the limestone treated soil has given a greater total yield of dry matter in every rotation with one exception. The apparent superiority of the limestone treated soil is due for the most part to the variation in the original fertility of the soil. If, therefore, the yields of the nearest check plot to each of the limed plots are considered rather than the average of all the checks, the actual difference in yields due to the two forms of lime becomes insignificant   Table 2 shows that the limestone plot has produced an average yield of dry matter of 956 pounds in excess of burned lime, however, if the differences in original fertility of these plots are considered as measured by the difference in yields of the nearest checks (36

and 24) the difference becomes only 268 pounds. A study of the probable error due to the variability of these plots as measured by Gardner, Noll, and Lewis (4) shows that the odds in favor of limestone are only 6 to 1. To be significant the odds should be at least 30 to 1.

A study of table 3 shows that at the end of the fifth rotation the burned lime treatment begins to outyield the untreated plots.

DETAILED STUDY OF THE LIMED AND UNLIMED SOILS OF EACH TIER OF PLOTS BASED ON THE 1921 SAMPLES (1881–1921)

The data secured from earlier studies of these old plots present evidence contrary to the results secured from various laboratory, field and greenhouse studies along similar lines as reviewed by Frear (3). The data secured from previous studies of the lime and limestone plots were the result of composite soils. Such investigations eliminated the possibility of securing information concerning any abnormal soil variation on an individual tier that might be responsible for the balance of nitrogen and organic carbon found in each preceding study to be present on the limestone treated soil in such amounts as not to be accounted for by the differences in yield. In the hope of throwing new light on the cause of the differences in organic carbon and nitrogen content between these limed soils and at the same time to add to our present knowledge concerning the reason for pronounced variations in the growth of the several crops on an individual plot, a detailed study of each plot of the series was undertaken in 1921 with reference to soil variability.

PLAN OF THE INVESTIGATION

Each plot was divided equally into nine areas by stretching strings across each tier of plots at intervals of 29.2 feet. Six borings were made in each of the nine areas and composited into one sample. Nine samples were therefore secured from each of the 144 plots totaling 1296, which will be referred to as sub-samples. Each sub-sample was then spread out on a sheet of paper arranged in the order secured in the field. This gave an excellent opportunity to study the variations in the color of the soil of each plot at 29.2 feet intervals.

Aside from the normal variation that would be expected on this residual soil of variable topography there appeared no abnormal condition on the plots of tiers 1, 2 and 3. When the sub-samples of tier 4 were arranged in order, however, it was at once seen that several plots on the south end of the tier showed abnormal changes in the color of the respective areas varying from the normal light brown of the Hagerstown series to black at the extreme south end. This condition was found on plots 32, 33, 34 (limestone), 35, and to a lesser degree plots 30, 31, and 36. The other plots including the burned lime soil showed a normal variation.

Black color due to charcoal

Examination of these black areas with special reference to the limestone soil disclosed the presence of particles of charcoal which varied from particles the size of a field pea to a finely divided powder thoroughly incorporated with the soil mass. The grass division strips which separate the plots were examined and found to show the same condition. The charcoal therefore has been present in the soil since some time prior to 1868 at which time the plots were laid out.

Probable source of the charcoal

Located within one mile of the plots still stands the remains of one of America's oldest charcoal iron furnaces, one of several located in Center County. This furnace was put into operation in 1792 and continued until 1809 and again from 1825 to 1858. Throughout this section of Center County were located charcoal pits operated to supply material for this and several other iron furnaces in this section of Pennsylvania. The charcoal found on the plots no doubt is the residue from one of these old pits.

VARIATIONS IN ORGANIC MATTER AND NITROGEN ON THE LIMESTONE PLOT OF
TIER 4 AS COMPARED TO THE BURNED LIME SOIL

Examination of the soil at each end of the two plots shows the influence of the incorporated charcoal on the organic carbon and nitrogen content of the limestone soil and the amount in excess of that found on the burned lime treated soil of this tier is sufficient to account for the difference between these two plots as shown in earlier studies.

The burned lime soil shows a variation of 264 pounds nitrogen per acre and 8613 pounds of organic matter per acre between the two ends of the plot as compared to 1006 and 128,229 pounds respectively in case of the limestone plot. The N–C ratio on the limestone plot varies from 1/11.83 to 1/29.11 as compared to 1/12.37 for the normal ratio shown in tables 5, 6 and 7.

The balance of nitrogen and carbon found on the limestone soil as shown by earlier studies including the four tiers may be accounted for by consideration of the difference shown in table 5 including also the small differences shown in tables 6, 7, and 8.

Reference to table 1 will show that the limestone soil apparently is increasing in organic matter as compared to the burned lime treatment. The actual differences in favor of limestone between the four periods of sampling are as follows: 6896, 7820, 9461, and 9913 pounds of organic matter, respectively. These differences are, however, due not to the actual accumulation of organic matter on the limestone treated soil as would naturally be inferred from the above figures, but to the difference in the methods of securing samples. The number of borings taken per plot at each sampling period was 5, 10, and 54 respectively. The charcoal deposit covers approximately forty per cent of the

limestone plot on tier 4. The amount of charcoal incorporated with the soil is greatest on area nine and gradually decreases until area six is reached wheie the soil appears normal. There is, however, no sharp line of demarcatic The increased number of borings taken at each succeeding period of study would include relatively more of the soil of area 9.

The question naturally arises in the mind of the reader as to why this charcoal was not earlier discovered. As stated before, the previous studies included a composite sample of the four tiers. The proportion of charcoal soil thus became relatively small. The small charcoal particles may be mistaken for partly decayed plant residues at the time the soil is prepared for analysis. The larger particles shown in the accompanying plate were originally coated

TABLE 4

Influence of the charcoal deposit on the organic carbon and nitrogen content of the limestone plot on tier 4

	TREATMENT	TOTAL NITROGEN PER ACRE		ORGANIC CARBON	ORGANIC MATTER PER ACRE	NITROGEN-CARBON RATIO
		per cent	*pounds*	*per cent*	*pounds*	
North End, 117 feet {	Burned lime	0 1118	2,236	1 2855	44,324	1 to 11.49
	Limestone	0.1305	2,610	1.5448	53,263	1 to 11.83
South End, 58 feet { (areas 8 and 9)	Burned lime	0.1250	2,500	1 5353	52,937	1 to 12.26
	Limestone	0 1808	3,616	5 2637	181,492	1 to 29 11

TABLE 5

TREATMENT	TOTAL NITROGEN PER ACRE		ORGANIC CARBON	ORANIC MATTER PER ACRE C × 1.724 × 2,000,000	N-C RATIO	AVERAGE N-C RATIO OF TIERS 1, 2, 3
	per cent	*pounds*	*per cent*	*pounds*		
Burned lime.......... ...	0.1133	2,266	1.360	46,983	1 to 12.00	1 to 12.75
Limestone...	0.1491	2,982	2.593	89,047	1 to 17.39	1 to 12.36

with fine silt and adhering clay and do not expose the fresh black surface in the manner shown. These particles may have easily been mistaken for gravel or small irregular stones found in abundance on the plots. Reference to the diagram of the plots will show the presence of the charcoal area indicated by small dots, the number of which are in proportion to the amount of charcoal present. A detailed soil survey was made to determine the proportion of the areas affected.

THE RELATIVE AMOUNTS OF ORGANIC MATTER AND NITROGEN FOUND ON PLOTS OF TIERS 1, 2, AND 3

After the soils had become air dried in the manner indicated, that representing each area was prepared for analysis by sifting through a 1-mm. screen in

the usual way. Aliquots of the nine areas were composited into one sample represeı ing the respective plot. The remainder of the soil of each area was reservc for future study. The sifted soil was ground to pass a 100-mesh screen.

ANALYTICAL METHODS

Total carbon was determined by the usual dry combustion method using a multiple unit electric furnace, mineral carbon by the dilute phosphoric acid method, nitrogen by the use of the Gunning method modified to include nitrate nitrogen. The Grandeau method, as described by Wiley (10), the estimation of alkali soluble humus.

TABLE 6

Organic carbon and nitrogen found on plots of tier 1

	PLOTS 1, 14, 24, 36 (UNTREATED)	PLOT 23 (BURNED LIME)	PLOT 24 (LIMESTONE)
Organic carbon, *per cent*	1.6534	1.7772	1.6888
	1.6411	1.7513	1.7104
	1.7409	1.7835	1.6874
	1 7191	1.7780	1.6709
Average	1.6886	1.7725	1.6894
Equivalent pounds per acre organic matter*	58,223	61,116	58,251
Nitrogen, *per cent*	0.1215	0.1294	0.1302
	0.1205	0.1288	0.1322
	0.1252	0.1312	0.1300
	0.1232	0.1312	0.1294
Average	0.1226	0.1302	0.1305
Equivalent pounds per acre	2452	2604	2610
Nitrogen—carbon ratio	1:12.61	1:13.74	1:12.97
	1:13.62	1:13.52	1:12.94
	1:13.89	1:13.59	1:12.95
	1:13.95	1:13.55	1:12.91
Average	1:13.77	1:13.61	1:12.97

* Organic C $\times$ 1.724 $\times$ 2,000,000.

Tables 6, 7, and 8 show the results secured when each tier was separately studied.

The data presented in tables 6, 7, and 8 and summarized in table 9 secured as the result of the 1921 investigations, show that the relationship between the burned lime and limestone soils is entirely contrary to the earlier studies. By elimination of the plots of tier 4 an opportunity is given for the first time to study the actual comparative effects of these two forms of lime. In drawing our conclusions we may consider each tier as a separate field on which have been applied 40,000 and 80,000 pounds per acre respectively of burned lime and pulverized limestone. Ten complete rotations have been completed in each case. At first only duplicate determinations were made by the junior

TABLE 7

Organic carbon and nitrogen found on plots of tier 2

	PLOTS 1, 14, 24, 36 (UNTREATED)	PLOT 23 (BURNED LIME)	PLOT 34 (LIMESTONE)
Organic carbon, *per cent*	1.3630	1.4406	1.4148
	1.3951	1.4210	1.4287
	1.4360	1.4475	1.4423
	1.3616	1.4169	1.4175
Average	1.3889	1.4315	1.4258
Equivalent pounds per acre organic matter	47,822	49,358	49,162
Nitrogen, *per cent*	0.1052	0.1162	0.1116
	0.1070	0.1133	0.1142
	0.1082	0.1192	0.1144
	0.1050	0.1122	0.1122
Average	0.1064	0.1152	0.1131
Equivalent pounds per acre	2128	2304	2262
Nitrogen—carbon ratio	1:12.95	1:12.39	1:12.68
	1:13.04	1:12.53	1:12.51
	1:13.27	1:12.15	1:12.61
	1:12.96	1:12.62	1:12.63
Average	1:13.05	1:12.43	1:12.61

TABLE 8

Organic carbon and nitrogen found on plots of tier 3

	PLOTS 1, 14, 24, 36 (UNTREATED)	PLOT 23 (BURNED LIME)	PLOT 34 (LIMESTONE)
Organic carbon, *per cent*	1.2449	1.2607	1.2438
	1.1729	1.2443	1.2247
	1.2340	1.2182	1.2451
	1.1579	1.2345	1.2206
Average	1.2024	1.2394	1.2336
Equivalent pounds per acre organic matter	41,459	42,735	42,535
Nitrogen, *per cent*	0.1002	0.1042	0.1088
	0.0990	0.1038	0.1072
	0.1000	0.1022	0.1094
	0.0982	0.1032	0.1072
Average	0.0994	0.1034	0.1083
Equivalent pounds per acre	1988	2068	2164
Nitrogen—carbon ratio	1:12.42	1:12.09	1:11.43
	1:11.85	1:11.99	1:11.42
	1:12.34	1:11.91	1:11.38
	1:11.79	1:11.96	1:11.38
Average	1:12.10	1:11.98	1:11.40

author. However, a study of the data brought out the fact that the actual differences in organic carbon and nitrogen content between the two plots were in some cases actually less than the difference between two closely checked determinations. It was thought advisable, therefore, to run a second duplicate set of determinations on the same samples and thus reduce the experimental error and at the same time afford an opportunity of making probable error studies. In each table, therefore, the average results are based on four separate determinations on the same sample.

A study of the results secured on the three series of plots shows that in each case the burned lime soil contains slightly more organic matter while the limestone plot shows a slight balance of nitrogen on tiers 1 and 3. The actual differences, however, are within the experimental error and the odds in each case as shown later are insignificant.

TABLE 9

Summary of tables 7, 8, and 9 showing the average results secured on the plots of tiers 1, 2, and 3

	PLOTS 1, 14, 24, 36 (UNTREATED)	PLOT 23 (BURNED LIME)	PLOT 34 (LIMESTONE)
Organic carbon, *per cent*.....................	1.4266	1.4811	1.4496
Equivalent organic matter, *pounds per acre*......	49,168	51,070	49,983
Nitrogen, *per cent*...........................	0.1094	0.1162	0.1172
Nitrogen, *pounds per acre*....................	2188	2324	2344
Nitrogen-carbon ratio.......................	1 to 13.04	1 to 12.75	1 to 12.37

THE SIGNIFICANCE OF THE DIFFERENCES IN ORGANIC CARBON AND NITROGEN AS AFFECTED BY LIMING[3]

As already stated, in connection with the studies of Hess, the comparatively small differences in organic carbon and nitrogen found in favor of the limestone treated soil were made the basis for rather exaggerated claims concerning the merits of limestone as compared with burned lime. In order, therefore, to safeguard the 1921 data it seems advisable to determine mathematically if the differences in organic carbon and nitrogen are really significant or rather if the odds are in favor of any one treatment.

If the means of the chemical determinations are taken, the odds may by "Students" method be computed in favor of the plots having the highest content of organic carbon or nitrogen. This method of interpreting experimental data and its application are fully discussed by Love and Brunsen (8) and by Love (7). From the mathematical study of the data presented in tables 6, 7, and 8, the following conclusions were drawn:

The odds indicate that the gound limestone and the burned lime plot are not significantly different in their content of organic carbon nor in content of nitrogen. When the limed plots

[3] The computations from which the conclusions are drawn were made by Dr. C. F. Noll of the Department of Agronomy.

are compared with the untreated check plots in content of organic carbon the burnt lime plot only seems significantly higher than the check plots. In nitrogen content both lime plots are significantly higher than the checks.

<div align="center">ALKALI SOLUBLE ORGANIC MATTER</div>

It has been shown conclusively that lime has a tendency to reduce the amount of alkali soluble organic matter in the soil as compared to the same soil unlimed. The degree of depression of the "matiere noire" should be greater, therefore, on soils where the more active forms of lime are applied. In order, therefore, to study the behavior of the two forms of lime under consideration which have been applied in excessive amounts, the organic matter soluble in 4 per cent NH_4OH was determined after first leaching the soils with 1 per cent HCl. The organic carbon was also determined on the alkali extract by evaporation in a copper boat and subsequent determination of carbon in electric furnace. Although a slight loss of carbon occurs as has been shown by

<div align="center">TABLE 10</div>

Alkali soluble organic matter and proportion of total organic carbon and nitrogen present in the extract, based on an average of tiers 1 and 3

	PLOTS 1, 14, 24, 36 (UNTREATED)	PLOT 23 (BURNED LIME)	PLOT 34 (LIMESTONE)
	per cent	*per cent*	*per cent*
Alkali soluble humus.........................	1.043	1.005	0.925
Alkali soluble nitrogen.......................	0.0610	0.055	0.0580
Alkali soluble carbon........................	0.3838	0.3764	0.3600
Total nitrogen soluble in NaOH..............	55.353	47.373	48.576
Total organic carbon soluble in NH_4OH........	27.278	24.994	24.726

Ames and Gaither (1) and by studies now in progress by the authors, the error should be distributed throughout the determinations. The nitrogen soluble in 3 per cent NaOH was also determined in the usual way.

The unlimed soil shows a higher percentage of alkali soluble organic matter, than either of the limed plots. The proportion of the total nitrogen and organic carbon soluble in alkali is also higher in this soil. A comparison of the two differently limed soils shows a higher proportion of carbon associated with the "humus" on the burned lime soil and a lesser proportion of nitrogen.

<div align="center">SUMMARY</div>

The following summation of facts is based on a study of the three differently treated plot soils at the end of forty years (1881–1921) of continuous cropping during which time 40,000 pounds of burned lime have been applied in one series in comparison with 80,000 pounds of pulverized limestone. Both limed soils are studied in relation to the untreated soil. The figures given are expressed on the acre basis (2,000,000 pounds).

1. The limestone soil contains as an average of the three tiers 20 pounds of nitrogen in excess of that found on the burned lime soil.

2. The burned lime treated soil contains organic matter in excess of the limestone treated soil as follows: tier 1, 2865 pounds, tier 2, 196 pounds; and tier 3, 200 pounds; average, 1087 pounds.

3. The limed soils contain as an average 1359 pounds of organic matter and 146 pounds of nitrogen in excess of that found on the untreated soil.

4. The N - C ratio of the three soils was found to be as follows: Untreated, 1/13.04, burned lime, 1/12.75, and limestone soil, 1/12.37.

5. Both limed soils show less alkali soluble humus than the untreated soil.

6. On the untreated soil 55.353 per cent of the total nitrogen is associated with the alkali soluble humus as compared with 47.975 per cent on the limed soils.

7. On the untreated soil 27.278 per cent of the total organic carbon is soluble in dilute ammonia as compared with 24.86 per cent on the limed soils.

8. The limestone treated soil has produced a total of 9560 pounds of air dry matter above that produced by the burned lime soil.   In spite of this fact the burned lime soil contains 1087 pounds of organic matter in excess of the limestone soil.

9. During the second half of the experiment (1901–1921) the burned lime soil shows a reduction in yield of 6.7 per cent as compared to 17.5 per cent for the limestone soil and 12.9 per cent on the untreated soil.

10. As an average for 40 years the limestone soil has given 8.3 per cent greater yields than the burned lime treatment.   At the same time the untreated plot (no. 36) nearest the limestone plot has produced yields 6.4 per cent in excess of the untreated plot (no. 24) adjoining the burned lime soil. The apparent increased yields of the limestone treatment above the burned lime soil is due, therefore, largely to the original difference in residual fertility.

Concerning the earlier studies made on these plots (1899, 1911 and 1915)

11. The origin of the idea concerning the destructive action of burned lime on soil organic matter is traced to the studies of Hess made in 1899.

12. The balance of nitrogen and organic carbon found on the limestone treated soil as the result of the earlier studies has been shown to have been derived from charcoal found on the limestone plot of tier 4.

13. The difference of 0.2 per cent of organic carbon and 0.0169 per cent nitrogen as found in the limestone soil as reported by Hess was computed by Hopkins to the equivalent of 75,200 and 75,000 pounds respectively of farm manure destroyed by the caustic action of burned lime.

14. The charcoal found on the limestone plot of tier 4 after having been incorporated in the soil for perhaps 75 years shows the following composition: organic carbon, 64.136 per cent; nitrogen, 0.25 per cent; loss on ignition (organic matter), 83.94 per cent; and ash, 16.06 per cent.

15. The charcoal was found to be present in sufficient quantity to furnish 47.55 per cent of the total organic carbon found on the plot. On the south end of the plot 70.8 per cent of the organic carbon was found to be derived from charcoal.

16. The condition and amount of the calcium applied as burned lime and limestone present in the soil after 40 years and the relative effect upon the ultimate reaction of the soil will be presented as the second of a series of papers dealing with a study of these old plots.

CONCLUSIONS

1. The determination of the experimental error of the 1921 data shows conclusively that there is no significant difference in the action of burned lime and limestone on soil organic matter at the end of 40 years of continuous treatment during which time the two forms of lime have been applied in amounts eight times that now recommended for soils of limestone origin.

2. Both the limestone and burned lime treated soils show a significant increase of nitrogen above that found on the untreated soil.

3. It has thus been shown that there is no evidence whatsoever to warrant the belief that burned or caustic lime has a destructive action on soil organic matter in excess of such action by lime carbonate. On the contrary, both forms of lime under the condition of this, the oldest lime experiment in existence, have conserved nitrogen and organic matter as compared to the untreated soil.

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PLATE

PLATE 1

FIG. 1. Coarse charcoal taken from the surface of the soil washed free from adhering soil.
FIG. 2. Color of soil of areas 8 and 9 where finely divided charcoal is incorporated with the surface soil.
FIG. 3. Normal soil.
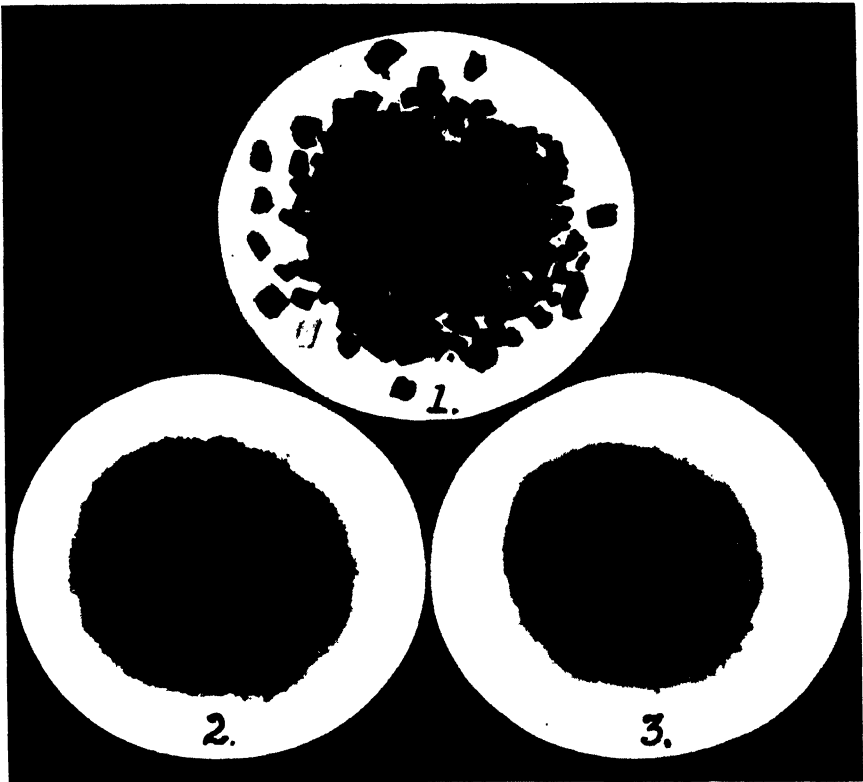
NITRIFICATION IN SOME SOUTH AFRICAN SOILS: PART II

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INTRODUCTION

Since fertilizer dealers and manufacturers in South Africa continue to press the sale of mixed fertilizers for general use in the areas of summer rainfall, despite contrary propaganda and advice from the Union Department of Agriculture, the writer has endeavored to obtain additional data to those already published by him regarding the intensity of nitrification in these soils (2). He has tried to obtain data which might help to illuminate, support or explain that fact so often noted in fertilizer experiments in this area, viz., that nitrogenous manures alone or in mixed fertilizers rarely give any increase in crop yields and when they do it is generally not a profitable one.

This department advises the use of a crop rotation including a legume together with phosphates applied to the grain crops, and the use of lime and potash only when necessary. The latter substances have been profitable rarely and generally only with crops of a limited root system.

On account of the low organic matter content of our soils, the low price of land and the high price of nitrogen, it is bad practice and also bad economics to apply nitrogen costing 1 shilling per pound in mixed fertilizer when it can be obtained more cheaply and in a more suitable form by means of legumes. In the area under discussion optimum soil temperature and rainfall occur together, and thus maximum nitrification can be expected at the time of greatest crop growth. The studies of this and the previous paper clearly indicate that this supposition is correct.

The studies hereafter recorded are in part a continuation and an extension of some of those already published, but some fresh aspects are also dealt with.

I. SEASONAL VARIATION IN NITRATE CONTENT

This is a continuation of the author's previous study (2). Samples for nitrate and moisture determinations were taken as described there. Only two strips of land were kept under observation; one, the cultivated fallow land and another, the uncultivated fallow land which was allowed to revert to grass and weeds during the twenty-one months that the nitrate and moisture was determined. The uncultivated fallow strip does not correspond to the virgin land previously studied, but gave a similar curve in the second summer

by which time it had become more compact, and thus less well aerated and capable of holding water.

A graphic representation of the results will be found in figure 1 which also shows the soil moisture at the time of sampling and the rainfall from December, 1920, to July, 1922.   For the soil and air temperatures during this period consult figure 2.   As was previously noted, soil moisture and rainfall appear to have a greater influence than temperature on the soil's nitrate content, although the soil temperature was never less than 47.70°F. during the two winters of the duration of this study, and thus was not low enough to stop nitrification, although it may have killed off the enemies of the nitrate bacteria.
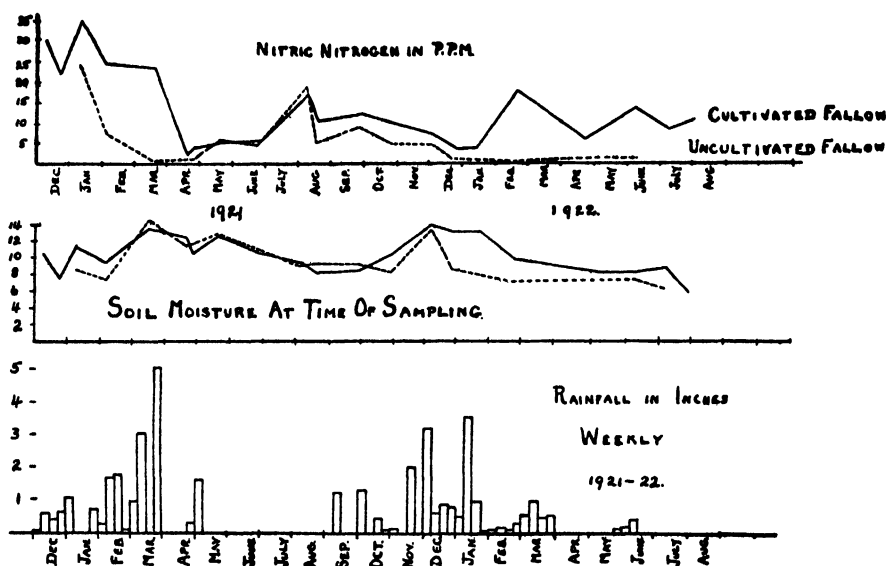
FIG. 1. A COMPARISON OF THE VARIATION IN NITRIC NITROGEN IN PARTS PER MILLION IN THE FIRST FOOT OF SOIL, WITH THE PER CENT OF SOIL MOISTURE AT THE TIME OF SAMPLING AND THE RAINFALL DURING THE SAME PERIOD

This is indicated by a rise in the nitrate curve in both winters after the commencement of the frosts.   It cannot, of course, be attributed solely to the cold as the soil at this time of the year is approaching its minimum moisture content.   This low moisture may in itself be sufficient to kill off the protozoa, but the upward tendency of the curve is shortly after the frosts and not after the soil has reached its minimum moisture content.

The influence of high temperature is difficult to gauge since it occurs nearly always around the period of greatest precipitation.

The influence of rainfall is more easily followed.   On three occasions there was a distinct rise in the nitrate content following an increase in soil moisture after rain.

The rapid fall in nitrate content in the cultivated fallow land in March 1921, is doubtlessly due to excessive leaching of these salts from the first foot of soil. There was over five inches of rainfall during the last week of that month.

The curve for the uncultivated fallow land nitrate shows a steep fall two and a half months earlier than the cultivated fallow land. This can be ascribed to the rapid growth of grasses which always occurs after the summer rains, and the consequent absorption of the soluble nitrates by their extensive root systems.

Despite a rapidly decreasing temperature there was an increase in nitrate nitrogen both in the cultivated and uncultivated fallow land following the light rains of late April and early May. It appears that more than three inches of rain are required to cause a loss of nitrate from the first foot of this soil by leaching.

After the frosts of June, there was a rapid increase in nitrates in both soils. This reached a maximum after the coldest weather in July 1921. The writer is of the opinion that this rise may have been due to an elimination of competing and predaceous flora by cold. During August there was a drop for which no explanation is offered. This was followed by a slight rise in September due possibly to the increase in soil moisture brought about by an inch of rain a week before the sample was taken. Some of this increase should be ascribed, perhaps to a rise in temperature during this period. From October to January both soils lost in nitrate content. The uncultivated fallow from November on lost more rapidly than the cultivated, due to the absorption of its nitrates by the growing vegetation. The summer rain and luxuriant vegetation compacted this soil so much that its subsequent behavior, due to the loss of its nitrates, poor aeration and dryness, was like that of the virgin soil reported earlier (2). Apparently, the rains in November, December and January, 1922, were too heavy to allow nitrates to accumulate in the first foot of soil. It is only after the rainfall decreased greatly at the end of January and the soil moisture also, that there was a rise in the nitrate content of the cultivated fallow soil. This may have been due to an optimum moisture content for nitrification aided by a capillary rise of nitrate from the lower soil. In spite of a well distributed rainfall of about 2 inches in March, 1922, there was again a fall in the nitrate curve of the cultivated fallow. After the light rains of late May and early June and the killing frosts in the latter month, there was again a decided rise in the nitrate curve. In July there was a fall followed by a rise in August corresponding to a fall in soil moisture and a rise in temperature.

The writer in his previous study of seasonal variation in this soil had noticed the rise in the nitrate curve after the first frosts and thought it suggested partial sterilization due to cold. A colleague who had some unpublished data on a smilar soil type a little further north showed the writer his curves of the nitrate content of the first, second and third foot of that soil, and also gave him his permission to mention them. These data showed an increase in the

nitrate content of the first foot of soil whenever there is a decrease in the second and third foot curves. He suggested interpreting the writer's data by the capillary rise of nitrates. The distinct rise following the frosts, however, appears to be more than a coincidence of capillary. The gravelly nature of the subsoil on this farm also is such as to exclude much of a possibility of a rise of nitrate in this manner. More detailed reasons are given in the next study on the soil wintered in various ways. The results of this study suggest that the writer's previous opinion of the cause of the rise after the frosts is correct.

The 1921–22 summer was one of the driest on record at this station and it shows up clearly in the low nitrate figures. The maximum nitrate content for the year was only 17 p.p.m. whereas in January 1921, there was a crest rising to 35 p.p.m., in January, 1920, 33 p.p.m. and in December, 1919, 49 p.p.m. of nitric nitrogen in the cultivated fallow land.
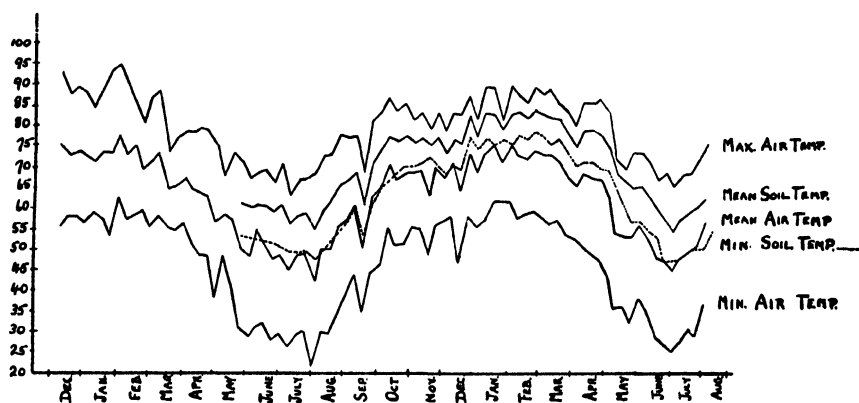
FIG. 2. A COMPARISON OF SOIL AND AIR TEMPERATURE DURING THE PERIOD OF THE DETER-
MINATION OF THE NITRIC NITROGEN, 1921–1922

The cultivated fallow land, due to the compaction and low moisture content of the soil after the grasses had matured, kept a low nitrate content until June when sampling was discontinued owing to the hardness of the soil. In the previous year the uncultivated fallow land was not so compacted and after the grasses on it had matured its curve clearly followed that of the cultivated fallow.

Soil moisture. There appears to be little difference between the moisture content of the cultivated and uncultivated fallow. During the summer of 1921–22, there was, however, a difference in favor of the cultivated soil. By this time the compaction of the uncultivated soil did not allow it to store so much water, and the grasses also used up much. The greatest difference is 3.2 per cent or about 64 tons per acre foot, enough to produce about 250 pounds more dry matter.

Soil temperature. This was taken every morning at 9 a.m. at the depth of 1 foot by means of an ordinary centigrade thermometer in a brass case which

fitted into a rubber stopper. The stopper was inserted into the mouth of a tube in the ground.

The writer is very pleased to see from Russell and Keen's data (6) that these readings may be taken as representative of the soil temperature at 6 inches below surface. Climatic conditions and radiation are, however, very different at this latitude and altitude from those at Rothamsted, and possibly the minimum may occur earlier. No self recording soil thermometer was available to record this. Russell and Keen also state that the soil temperature at 12 inches, if averaged with the air maximum, gives about the correct soil mean. This average has thus been calculated and plotted in figure 2, along with the air maximum, mean, and minimum and the soil minimum temperatures. The soil minimum temperature is for the most part 1–4°F. higher than the air mean temperature. The soil mean temperature calculated according to Russell and Keen, and over a period of 55 weeks, from the week ending May 24, 1921, to week ending July 31, 1922, was 69.9°F. The mean air average for the same period was 58.8°F. An average difference of 11.1°F. is thus in favor of the soil. The average soil and air minimum temperatures for the same period were 63.4°F. and 43.3°F. respectively, a difference of 20.1°F in favor of the soil population. In some cases the soil was actually 26°F. warmer than the air minimum. Russell and Keene show a difference of 10.8–14.4°F. between their air and soil minimums in favor of the latter.

The drop in soil temperature before winter and the rise after that season gives steep curves. The drop in September, 1921, is probably due to the rain, and in November, December, and March to the same cause. The cooling effect of rain on the soil temperature is more easily seen on the daily temperature sheets.

On an average of thirty-four determinations the, cultivated fallow land was 1.62°F. warmer than the uncultivated.

Conclusions

1. The factors which appear to have influenced the nitrate content of the first foot of soil most strikingly are the leaching effects of heavy rain and the favorable effect of light rain and adequate soil moisture.

2. Aeration also plays an important part, which is apparent in the low nitrate content of the uncultivated fallow soil in the months following the maturity of the grasses, when active growth can no longer be held responsible for the low nitrate content.

3. Temperature appears to play only a small part under our conditions, but it is a difficult factor to judge since it reaches a maximum at the time of maximum rainfall. The cold in early winter appears to stimulate the nitrification process. The soil minimum temperature during two winters was not below 47.7°F. This was not low enough to completely stop nitrification while moisture was adequate.

4. As regards the soil moisture of the cultivated and uncultivated fallow, there is not the difference in favor of the former that agricultural practice would lead one to expect. It is not until the second season when the vegetation is thoroughly established and the soil is compacted that its moisture content is clearly lower.

5. The average minimum of the soil temperature on this station was 20.1°F. higher than air average minimum a few feet away. The soil mean average was 11.1°F. higher than the air mean average, and the soil minimum 1–4°F. higher than the air mean. The living conditions for the soil flora are decidedly more favorable and temperate than the conditions pertaining outside it for other organisms.

6. The amount of soluble nitrogen present during the growing season in the surface foot of the soil studied, would appear to indicate that there is adequate for most crop requirements. It also seems to explain the reason why nitrogenous fertilizers have not given satisfactory returns.

II. NITRIFYING POWER OF SOIL WINTERED IN VARIOUS WAYS

This study was initiated to throw some light on the decided rise in nitrates after the frost as observed in this and in the previous paper (2). The possibility of capillary attraction has been brought up, but it seems strange that this should be so evident only after the frosts have commenced. There may be some capillary attraction but the nature of the lower strata of soil is such as to preclude much possibility of capillary attraction. There is a gravelly subsoil to be found at depths of 18–24 inches. Actual samples were taken down to a depth of 6 feet and the different 1-foot samples superimposed on one another in correct order in a glass tube one inch in diameter. Even under such favorable conditions and from a free water table there was no capillary rise over 6 inches. The third, fourth and fifth feet contained 63, 56 and 44 per cent of coarse gravel respectively. The writer does not wish it to be thought that he does not believe there is any chance of capillary attraction; there may be some from the second foot upwards, but he thinks from the exceedingly well drained subsoil and the low moisture content during winter, that the possibility of a capillary rise of nitrates is remote.

In order to ascertain if the cold weather did not improve the nitrifying capabilities of this soil, representative samples of the cultivated and uncultivated fallow were taken, and each lot divided into two portions. Twelve pounds were placed in glazed porcelain jars which had loosely fitting glazed covers. Two were buried in the field from which the samples were taken, and two were covered and kept in a fume free room in the laboratory from April 25, 1921, to August 22, 1921, when the soils were incubated as shown in table 1 together with field samples from the same places taken on August 17. All six samples were air dried before starting the incubation test. The soils were incubated alone in duplicate, and also with cowpea hay, dried blood, and ammonium sulfate, enough of these being added to give 7 mgm. of nitrifiable nitrogen to every 100 gm. of soil.

Table 1 indicates that:

1. The soil, whether cultivated or uncultivated, had better nitrifying powers after having been exposed to the cold.

2. The soil buried in pots in the field for the most part nitrified better than the soil buried in pots in the laboratory. The differences are, however, not sufficiently great to be very conclusive.

TABLE 1

Nitrification in soil wintered in different ways

NATURE OF THE SOIL AND WINTERING	SOIL ALONE				COWPEA HAY			DRIED BLOOD			AMMONIUM SULPHATE			SUMMARY OF ALL NITRIC NITROGEN INCREASES
	Nitric nitrogen at start	After 30 days	Increase in nitric nitrogen	Soil nitrogen nitrified	Total nitric nitrogen	Increase over soil nitric nitrogen	Added nitrogen nitrified	Total nitric nitrogen	Increase over soil nitric nitrogen	Added nitrogen nitrified	Total nitric nitrogen	Increase over soil nitric nitrogen	Added nitrogen nitrified	
	p.p.m.	p.p.m.	p.p.m.	per cent	p.p.m.	p.p.m.	per cent	p.p.m.	p.p.m.	per cent	p.p.m.	p.p.m.	per cent	p.p.m.
Cultivated fallow in pot in field..........	6.5	27.8	21.3	2.0	55.6	27.8	39.7	80.3	52.5	75.0	48.0	20.2	28.8	132.5
Cultivated fallow in pot in laboratory......	7.5	31.6	24.1	2.2	45.2	13.6	19.4	73.1	41.5	59.2	43.5	11.9	17.0	91.1
Cultivated fallow field sample, August, 1921..	10.9	40.6	29.7	2.8	73.0	32.4	46.2	72.0	31.4	47.7	99.0	58.4	83.4	151.9
Uncultivated fallow in pot in field........	3.4	43.6	40.2	3.9	64.7	21.1	30.1	99.2	55.6	79.4	100.2	56.6	80.8	173.5
Uncultivated fallow in pot in laboratory......	4.4	28.1	23.7	2.3	49.1	21.0	30.0	72.8	44.7	63.8	47.4	19.3	27.5	108.7
Uncultivated field sample, August, 1921......	4.1	26.4	22.3	2.1	58.5	32.1	45.8	82.7	56.3	80.4	81.5	55.1	78.7	165.8

3. The field soils, still more exposed under natural conditions to cold and drying influences, appear to have nitrified somewhat better than the soils in the pots.

4. There appears to be a slight indication that the uncultivated fallow soil nitrified better than the cultivated fallow. It may be that compaction and consequent bad aeration is another factor favoring partial sterilization and subsequent improved nitrification.

5. Two-thirds of the determinations on both cultivated and uncultivated soil showed more nitrates in the soil wintered normally and naturally than in those which were buried in pots to the depth of a foot. The soils in pots did not become as dry as the field soils.

6. The foregoing results in general appear to indicate that the rise in the nitrate curve after the cold weather sets in, may be due to better conditions for the nitrifying bacteria. The data is, however, not conclusive enough to be satisfactory.

A sample of the field soils taken after the coldest winter period, showed no active protozoa. This determination was kindly made by Miss E. Taylor of the University of Witwatersrand.

III. THE NITRIFYING POWER OF VARIOUS DEPTHS OF CULTIVATED AND UNCULTIVATED SOIL

These depth samples were taken and treated as described in part VII of the previous paper, except that the incubation took place in one-pound glass mason jars instead of tins, and in an incubator at 28–30°C. for thirty days instead of in an open room. To the soils were added dried blood, bone dust, ammonium sulfate and ground black jack-hay (*Bidens pilosa*) in amounts so as to add 7 mgm. of nitrifiable nitrogen per 100 gm. of dry soil. This soil type has already been described—a brown sandy soil with an appreciable amount of clay and containing a very gravelly limonite subsoil derived from basic igneous rocks below. The data in table 2 appear to confirm the previous study on this soil and indicate that little nitrification takes place below the first foot. There appear to be indications of some nitrification in every foot of the cultivated fallow, but the increases are so small as to be hardly reliably significant. In this uncultivated fallow there is no nitrification in the fourth foot, a little in the fifth, but none in the sixth foot.

Of the added fertilizers the best nitrified was the ammonium sulfate and the worst the black jack-hay, taking the results through all the 6 feet of both lots of soil.

General nitrification in the first foot of soil, was greater in the uncultivated fallow than in the cultivated fallow. The amount of nitrate reached in thirty days was, however, slightly less than had been actually ascertained from a field sample three weeks after this same land in grass had been ploughed up.

Conclusions

1. This study confirms number 7 of the previous paper and shows that relatively little nitrification occurs in the samples taken below the first foot.

2. The nitrifying power as evidenced by the nitrification of added nitrogenous fertilizers is also low below the first foot samples.

3. The total soil nitrogen decreases regularly from the first to the sixth foot in both soils (see fig. 3).

TABLE 2

Nitrifying power of various depths of soil

	SOIL ALONE				AMMONIUM SULPATE			DRIED BLOOD			BONE DUST			BLACK JACK HAY		
DEPTH OF SOIL (feet)	Nitric nitrogen at start (p.p.m.)	Nitric nitrogen after 30 days (p.p.m.)	Increase or decrease (p.p.m.)	Soil nitrogen nitrified (per cent)	Total nitric nitrogen (p.p.m.)	Increase over soil nitrogen alone (p.p.m.)	Added nitrogen nitrified (per cent)	Total nitric nitrogen (p.p.m.)	Increase over soil nitrogen alone (p.p.m.)	Added nitrogen nitrified (per cent)	Total nitric nitrogen (p.p.m.)	Increase over soil nitrogen alone (p.p.m.)	Added nitrogen nitrified (per cent)	Total nitric nitrogen (p.p.m.)	Increase over soil nitrogen alone (p.p.m.)	Added nitrogen nitrified (per cent)
Cultivated fallow																
1	2.1	29.9	27.8	2.3	50.4	20.5	29.2	72.5	42.6	60.8	50.5	20.6	29.4	8.5	*	0.0
2	3.3	11.7	8.4	0.8	5.8	*	0.0	22.7	11.0	15.7	5.1	0.7	1.0	4.6	*	0.0
3	9.4	7.3	*	0.02	11.2	3.9	5.5	3.7	*	0.0	8.0	*	0.0	6.2	*	0.0
4	5.2	5.4	0.2	0.4	4.8	*	0.0	4.9	*	0.0	4.1	*	0.0	6.9	1.5	2.1
5	1.6	4.3	2.7	0.4	4.4	0.1	0.1	1.6	*	0.0	1.8	*	0.0	2.1	*	0.0
6	2.6	3.4	0.8	0.2	5.8	2.4	3.4	0.9	*	0.0	1.6	*	0.0	3.3	*	0.0
Uncultivated fallow																
1	0.7	36.6	35.8	2.9	78.0	42.2	60.2	13.2	*	0.0	55.3	19.5	29.1	34.6	1.1	1.5
2	1.1	3.0	1.9	0.2	1.1	*	0.0	2.7	*	0.0	3.9	0.9	1.2	4.1	*	0.0
3	3.8	2.9	*	0.0	4.3	1.4	2.0	2.7	*	0.0	3.0	0.1	0.1	1.7	*	0.0
4	4.1	5.1	1.0	0.01	4.6	*	0.0	1.4	*	0.0	0.7	*	0.0	1.8	*	0.0
5	3.8	2.9	*	0.0	2.8	*	0.0	3.2	0.3	0.4	1.9	*	0.0	1.5	*	0.0
6	4.1	5.2	1.1	0.3	5.2	†	0.0	3.9	*	0.0	5.0	*	0.0	2.8	*	0.0

*Decrease.
†No change.

IV. A COMPARISON OF THE NITRATE CONTENT OF SOIL BEFORE AND AFTER
DRYING IN THE LABORATORY

It has now long been an established fact that if a soil is air-dried in the
laboratory and then subjected to nitrification tests it gives better results than
the same soil not allowed to dry (1). If a soil is however, not required for
nitrifying tests, but merely for a determination of its nitric nitrogen, is the
result affected much by allowing it to become air-dried in the laboratory?
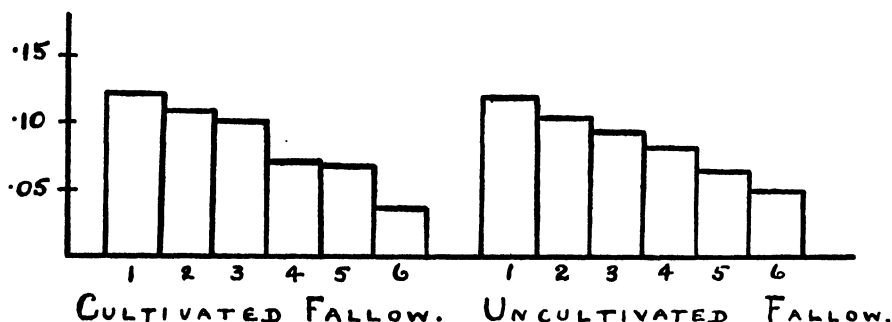
FIG. 3. PER CENT NITROGEN IN FIRST 6 FEET OF SOIL

TABLE 3

Nitrate content before and after drying for twenty-eight days

SOIL DEPTH	CULTIVATED FALLOW, APRIL 19, 1921	CULTIVATED FALLOW, 28 DAYS LATER	CHANGE	UNCULTIVATED FALLOW, APRIL 20, 1921	UNCULTIVATED FALLOW, 28 DAYS LATER	CHANGE
feet	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1	2.1	2.3	0.2	0.7	0.6	−0.1
2	3.3	5.2	1.9	1.1	0.6	−0.5
3	9.4	7.4	−2.0	3.8	2.6	−1.2
4	5.2	4.9	−0.3	4.1	3.3	−0.8
5	1.6	2.4	0.8	3.8	3.9	0.1
6	2.6	3.0	0.4	4.1	4.3	0.2
Total.....	24.2	25.2	1.0	17.6	15.3	−2.3
Average...	4.03	4.2	0.17	2.93	2.55	−0.38

To ascertain this, the nitrate content of twelve samples was determined
immediately after sampling and again after 28 days of air drying thinly spread
on clean brown paper with the following results. All the figures are as nitric
nitrogen in parts per million, in table 3.

The average difference is so small as to be well within the experimental
error. It would seem then that if it is not convenient to determine the nitric
nitrogen when a soil arrives, it can safely be done later if the soil has been
spread out thinly to dry.

V. NITRIFICATION IN ACID SOILS

In the writer's previous work it was noted that a number of soils of high lime requirement according to the Veitch Method yet nitrified their own and added nitrogen very efficiently. The writer decided to study three of the soils with the greatest lime requirement in somewhat more detail (3). Throughout this study, the term "acid" means lack of base as indicated by the Veitch lime requirement method. This is a phase of the subject that has received little attention and yet is of great economic importance, especially with low priced land. The soils used are described in table 4.

It is an established fact that liming on acid soil usually increases nitrification, but whereas it may do so profitably on land worth £50 to £250 per acre, it is a different proposition when the land values are 10 shillings to £20, and ground limestone at 11 shillings to 22 shillings 6 pence per short ton.

Another very important factor must be borne in mind when dealing with South African soil problems, and that is their very low phosphate content. Until such deficiency is remedied liming, however cheaply done, can never be

TABLE 4

Three types of acid soils

SOIL NUMBER	SOIL TYPE	WATER HOLDING CAPACITY	VEITCH LIME RE-QUIREMENT ($CaCO_3$)	TOTAL NITROGEN
		per cent	*pounds*	*per cent*
1	Black peaty clay loam................	125	3740	0.64
2	Brown sandy loam...................	37	3713	0.05
3	Brown loam........................	64	6473	0.27

profitable investment for the land owner, even though it should greatly stimulate nitrification. Liming, however, even with carbonate of lime greatly improves a soil physically and must sometimes be considered from the economic standpoint. For Russell and Keen (7) show that there was no increase in crops from the heavy chalking of wheat, oats or potatoes, although the land has greatly benefitted physically as shown by lower draw-bar pull, smaller draught per pound, and more miles per hour ploughed.

Object of this investigation

With the above facts in mind it was decided to see whether lime in the form of ground limestone stimulated nitrification in the above mentioned soils, and if it did so profitably.

The soils were incubated as usual in glass jars, after the lime and fertilizers had been added and water at the rate of 70 per cent of the soil's water-holding capacity.

Carbonate of lime, amonium sulfate and superphosphate (acidity calculated as H_2SO_4 was 0.5 per cent) were added in the amounts detailed in

tables 5 to 7. The superphosphate and lime were sprinkled on the top of the 100 gm. of soil in their respective jars and then stirred in.

When both had to be applied to the same soil, first the superphosphate was sprinkled on top then the ground limestone, and both were stirred in together. The ammonium sulfate was in all cases added in solution when the water content was being made up. The figures in tables 5 to 8 are averages.

Soil no. 1 shows very fair nitrifying power which lime has stimulated comparatively little. The limestone at the rate of 1 ton per acre has given most profitable results in this class of treatment. The acid phosphate has stimu-

TABLE 5

Nitrification in acid soil no. 1 (lime requirement 3740 pounds)

TREATMENT PER ACRE	NITRIC NITROGEN	INCREASE OVER SOIL NITRIC NITROGEN	COST OF TREATMENT PER ACRE	VALUES OF INCREASED NITRIC NITROGEN PER ACRE	GAIN OR LOSS PER ACRE
	p.p.m.	*p.p.m.*	*shillings*	*shillings*	*shillings*
Soil alone before incubation....................	28.1	—			
Soil alone after incubation....................	116.8	—			
1,000 pounds lime*.........................	90.6	Loss	10	Loss	−10
2,000 pounds lime..........................	124.8	8.0	20	24	4
4,000 pounds lime..........................	128.7	11.9	40	35.7	−4.3
15,000 pounds lime..........................	140.2	23.4	150	70.2	−79.8
1,000 pounds superphosphate...............	139.7	22.9	55	67.7	12.7
1,000 pounds superphosphate, 1,000 pounds lime......................................	157.1	40.3	65	120.9	55.9
1,333 pounds ammonium sulfate.............	193.4	76.6	333	229.8	−103.4
1,333 pounds ammonium sulfate, 1,000 pounds lime.......................	237.3	120.7	343	362.1	19.1
1,333 pounds ammonium sulfate, 15,000 pounds lime......................................	237.3	120.5	483	361.5	−121.5
1,333 pounds ammonium sulfate, 8,000 pounds lime......................................	227.3	110.5	413	331.5	−81.5

* In form of ground limestone.

lated nitrification even more than the limestone also more profitably. As phosphate is one of the greatest requirements of this soil there is every likelihood that field results from crop growth would be even more striking. The addition of 1000 pounds of limestone with the superphosphate has stimulated nitrification even more and given the most profitable nitric nitrogen return of the series. The ammonium sulfate has been excellently changed, in fact just shows over a 100 per cent of the added nitrogen nitrified. One thousand pounds of lime added to this has again stimulated nitrificaton profitably, but the heavier applications have not improved it any further. (See table 5)

It appears then that this soil, although showing excellent nitrification, would yet show further profitable increases when 1000 pounds of limestone was added with acid phosphate and ammonium sulfate.

The acid phosphate has stimulated nitrification. This observation concerning phosphates, both rock and acid, has also been made previously by other workers (5) (9).

Nitrification in soil no. 2 is very poor and the actual differences in determinations so small that no satisfactory conclusions can be derived therefrom. Large quantities of limestone have, however, not benefitted nitrification profitably. (See table 6)

TABLE 6

Nitrification in acid soil 2 (lime requirements 3713 pounds)

TREATMENT PER ACRE	NITRIC NITROGEN	INCREASE OVER SOIL NITRIC NITROGEN	COST OF TREATMENT PER ACRE	VALUE OF INCREASED NITRIC NITROGEN PER ACRE	LOSS PER ACRE
	p.p.m.	*p.p.m.*	*shillings*	*shillings*	*shillings*
Soil alone before incubation....................	4.7	—	—	—	—
Soil alone after incubation....................	7.7	—	—	—	—
1,000 pounds lime*.........................	9.5	1.8	10	7.2	2.8
2,000 pounds lime.........................	10.4	2.7	20	10.8	9.2
4,000 pounds lime.........................	8.0	0.3	40	1.2	38.8
15,000 pounds lime.........................	14.1	6.4	150	25.6	124.4
1,000 pounds superphosphate................	7.9	0.2	55	0.8	54.2
1,000 pounds superphosphate, 1,000 pounds lime....................................	8.7	1.0	65	4.0	61
1,333 pounds ammonium sulfate............	4.4	Loss	333	None	333
1,333 pounds ammonium sulfate, 1,000 pounds lime....................................	4.1	Loss	343	None	343
1,333 pounds ammonium sulfate, 15,000 pounds lime....................................	21.4	13.7	483	54.8	428
1,333 pounds ammonium sulfate, 8,000 pounds lime....................................	9.7	2.0	413	8.0	805

* In form of ground limestone.

Nitrification in soil no. 3 is relatively better than that in no. 1 since 2.4 per cent of the total soil nitrogen was nitrified whereas only 1.3 per cent was nitrified in soil 1 and 0.6 per cent in soil 2. Here again limestone has not improved nitrification, but superphosphate seems to have slightly depressed it. The ammonium sulfate has been nitrified to the extent of 35 per cent of the added nitrogen in thirty days. The addition of limestone, however, does not appear to have improved matters. The one result certainly appears unreliable. In the above studies no value has been assigned to the nitrified ammoniacal residue, although this nitrogen is still worth 1 shilling

per pound.   The figures show that the limestone in the majority of cases did not help nitrification, and it was for some definite information on this point that the writer was seeking.   (See table 7)

Conclusions

1. Even in soils of high lime requirements, nitrification can be adequate for crop production. In two of the soils it is quite up to average of all the soils tested by the writer.

2. The addition of limestone alone has been profitable only in one instance. In the soil that nitrified badly, limestone did not help matters at all.

TABLE 7

Nitrification in acid soil 3 (lime requirement 6473 pounds)

TREATMENT PER ACRE	NITRIC NITROGEN	INCREASE OVER SOIL NITRIC NITROGEN	COST OF TREATMENT PER ACRE	VALUE OF INCREASED NITRIC NITROGEN PER ACRE TOOT	LOSS PER ACRE
	p.p.m.	*p.p.m.*	*shillings*	*shillings*	*shillings*
Soil alone before incubation.....................	8.8	—	—	—	—
Soil alone after incubation.....................	75.2	—	—	—	—
1,000 pounds lime*.........................	77.2	2.0	10	7.0	3
2,000 pounds lime..........................	78.7	3.5	20	12.3	7.7
4,000 pounds lime..........................	81.7	6.5	40	22.8	17.2
15,000 pounds lime..........................	75.5	0.3	150	11.0	139.5
1,000 pounds superphosphate................	60.3	Loss	55	None	55
1,000 pounds superphosphate, 1,000 pounds lime......................................	71.1	Loss	65	None	65
1,333 pounds ammonium sulfate.............	99.2	24.0	333	84	249
1,333 pounds ammonium sulfate,1,000 pounds lime......................................	63.9	Loss	343	None	343
1,333 pounds ammonium sulfate, 15,000 pounds lime......................................	91.3	16.1	483	56.4	426.6
1,333 pounds ammonium sulfate, 8,000 pounds lime............	101.4	26.2	413	91.7	321.3

* In form of ground limestone.

3. In one instance 1000 pounds of limestone has profitably stimulated nitrification where ammonium sulfate was applied, but the heavier dressings of limestone did not improve this process any more.

4. In three instances the addition of 1000 pounds of limestone where 1000 pounds of superphosphate has been applied appears to have stimulated nitrification.

5. In one instance 1000 pounds of superphosphate actually appears to have stimulated nitrification, in one instance not affected it and in one instance apparently depressed it.

6. It would seem, then, that on acid soils, using nitrification as the criterion, applications of limestone would hardly be profitable especially in large amounts. Field trials, however, might show some other benefits from limes. These soils are more acid than the average the writer has tested.

Boussingault and Breal noticed that forest and meadow soils did not contain nitrates and suggest soil acidity as the reason.   The writer has not examined forest soils, but has already remarked on the paucity of nitrates in land under natural grass.   When this virgin land had been ploughed up, however, there was found three weeks later 30 p.p.m. of nitric nitrogen in soil with a lime requirement of 1000 pounds per acre.   Is not the cause as far as the grass lands are concerned, rather that the compaction of the soil brings about poor aeration and that the little nitrate that is produced is readily used up matted numerous grass roots?

VI. NITRIFICATION IN RUSTENBURG TOBACCO SOILS

The soils were collected by the writer in connection with some work on soil type and composition as affecting the nicotine and ash contents and the quality of tobaccos.   Eight soils and their corresponding subsoils were sampled to the depth of one and two feet respectively.   They comprise three main types, a red loam, changing to a red clay loam, or black clay loam containing about 1.5 per cent of carbonate of lime and a light brown sandy loam.   Two of the types, although not containing sufficient carbonate of lime to be detected are alkaline in reaction.

Although the majority of the soils are poor in organic matter and nitrogen, it will be noticed that the percentage of soil notrogen nitrified is fairly satisfactory.   All details are given in table 8.

The black clay loams, despite their free lime, did not nitrify their soil nitrogen any better than the red clay loams.   The average percentage of soil nitrogen nitrified including soil and subsoil in each class was 3.85 per cent. The brown sandy loams had the poorest organic matter content, and the lowest water-holding capacity, and they also gave the poorest nitrification results.   The limed soil 8 from the Rustenberg Experiment Farm had been limed seven years previously, whereas the unlimed soil 7, which had not, gave slightly better nitrification results.

It is also noteworthy that out of eight soils and eight subsoils, with three exceptions, the subsoils produced most nitrates.   Approximately 107 pounds are removed by 3500 pounds of tobacco leaf and stalk of nitrogen.   On five of the soils, i.e., all excepting the brown sandy loams, nitrification appears to be quite adequate to meet such a demand, but the organic matter and nitrogen content of the soil would have to be maintained and improved, as in no instance is it very good.

Even on the sandy type, enough nitrate nitrogen might be produced during the growing season to meet the demands of the tobacco plant, but it would seem wiser to add an additional amount of nitrogen.

GENERAL CONCLUSIONS

The writer's studies on the nitrifying powers of thirty soils from various parts from the Transvaal as reported in this paper make him retain his former

opinions, that nitrification in these South African soils is not as active as Lipman and his co-workers found it to be on Californian soils and soils from the more humid portions of North America. Whereas, the author had previously found no soil here which had nitrified more than 5.2 per cent of its own nitrogen in 30 days at 28–30°C., he now has found one of granitic origin which nitrified 7 per cent of its own nitrogen in this time, despite its having a

TABLE 8

Nitrification in Rustenburg tobacco soil

SOIL TYPE AND NUMBER	WATER-HOLDING CAPACITY	REACTION OR CALCIUM CARBONATE	ORGANIC MATTER LOST ON IGNITION	NITROGEN	NITRIC NITROGEN AT START	NITRIC NITROGEN AT FINISH	INCREASE ON NITRIC NITROGEN	SOIL NITROGEN NITRIFIED	NITRATE NITROGEN PRODUCED PER ACRE FOOT
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*pounds*
Red Clay Loam:									
Naude 1......................	41	Alk.	4.19	0.103	1.4	36.2	34.8	3.3	144.8
Naude 1, subsoil..............	41	Alk.	6.44	0.068	1.3	26.5	25.2	3.7	106.0
Penzhorn 2...................	35	Alk.	4.45	0.065	2.0	39.7	37.7	5.8	158.8
Penzhorn 2, subsoil...........	41	Alk.	4.15	0 059	2.0	17.5	15.5	2.6	70 0
Black Clay Loam:									
Combrink 3...................	60	1.5	5.32	0.081	1.9	35.4	33.5	4.1	141.6
Combrink 3, subsoil...........	61	1.5	5.74	0.067	1.5	46.7	45.2	6.7	186.8
Combrink 4,..................	53	0.6	10.62	0.123	2.0	28.4	26.3	2.1	113.6
Combrink 4, subsoil...........	57	9.0	5.22	0.063	1.6	26.2	24.6	3.9	104.8
Rustenburg Experiment Farm 5...	66	1.3	4.98	0.085	2.2	25.2	23.0	2.7	100.8
Rustenburg Experiment Farm 5, subsoil.....................	60	1.45	5.7	0.073	2.1	28.4	26.3	3.6	113.6
Brown Sandy Loam:									
Rustenburg Experiment Farm 6...									
Rustenburg Experiment Farm 6, subsoil	37 / 39	Neut. / Neut.	3.82 / 4.94	0.074 / 0.056	1.8 / 1.3	11.4 / 11.9	9.6 / 10.6	1.2 / 1.8	45.6 / 47.6
Rustenburg Experiment Farm 7, unlimed......................									
Rustenburg Experiment Farm 7, unlimed......................	31	Neut.	2.24	0.081	2.7	16.0	13.3	1.6	64.0
Rustenburg Experiment Farm 8 limed.......................	36 / 32	Neut. / Sl. Alk.	3.72 / 2.28	0.067 / 0.092	2.0 / 3.3	17.7 / 17.9	15.7 / 14.6	2.3 / 1.5	70.8 / 71.6
Rustenburg Exp. Farm 8, limed subsoil.....................	37	Sl. Alk.	3.41	0.081	3.0	13.3	10.3	1.3	53.2

lime requirement of 2455 pounds per acre and a total lime content of only 0.14 per cent as calcium oxide. It did not, however, nitrify added nitrogenous fertilizers very well. The tables concerning the majority of soils which are more of local than general interest have been recently published elsewhere (4). The data, however, show fairly good nitrification quite adequate for our crop production. The only thing necessary is to maintain the organic matter and

so keep available a cheap supply of organic nitrogen for nitrification. Briefly the chief observations on the particular studies are as follows:

1. Moisture and aeration appear to be factors influencing nitrification under these climatic conditions more than temperature.

2. The seasonal variation study shows a nitrate production which would be adequate for most crops on this soil type and serves to throw light on the reason for the poor results from added nitrogenous fertilizers.

3. The drying of the soil in winter and also the frost appear to improve its nitrifying powers, when conditions again become favorable for nitrification.

4. In this soil type there was very little nitrification in samples taken below the first foot, although traces of activity could be found to the sixth foot in cultivated fallow, but the amounts are too small to be significant.

5. For a nitrate determination only, a soil sample can be allowed to dry out if thinly spread in the laboratory, without the nitrate content being appreciably affected.

6. Nitrification in two of the three acid soils studied was quite good, and not much improved by liming.

7. Nitrification in the Rustenburg tobacco soils was with the exception of two soil types satisfactory. In most cases the subsoils nitrified better than the surface soils.

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ALKALI SOIL INVESTIGATIONS: IV. CHEMICAL AND BIOLOGICAL EFFECTS OF TREATMENTS[1]

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The basis for discussion of the chemical effects in this paper is a second series of experiments conducted primarily with the purpose to study diffusion effects. In some of the cultures, therefore, the sulfur was mixed with the bulk of the soil; in some, only with the surface 4 inches. For a detailed discussion of the chemical effects the third paper (4) of this series should be consulted. The data of the second series only substantiate the results of the first series of experiments. However, the slight modification in the treatments, the use of distilled water, the temperature of incubation (room temperature instead of greenhouse temperature as in the first series of experiments) and the exclusive use of glazed earthenware pots introduced some features not discussed in the third paper, and these will be taken up presently.

Table 1 gives the scheme of the treatments.

Tables 2 to 11, inclusive, give the results. The procedure of obtaining the leachings and extracts was the same as in the first series. It should be noted that the extracts in this series were made on leached cultures (except as shown in table 10), while in the first series they were made on unleached samples.

CHEMICAL EFFECTS

Reaction

Invariably the reaction of the extracts was less alkaline than that of the leachings. This may be attribute to the efficiency of the leaching operations and to the rapid rate of oxidation of the sulfur during the period of drying the leached cultures previous to extraction, which had to be done on air-dried soil. The alkalinity did not disappear in this series as fast as in the first series. The slight variations in procedure, particularly temperature, was responsible for the slower rate. The factor of adding the sulfur to the surface instead of mixing it with the bulk of soil had some slight effect on the reaction of both the leachings and extracts. The acid reaction—pH 6.4—of culture 7 (table 11) is of interest: it may show that the soil is becoming unsaturated, i.e. all the replaceable bases have been forced out. [See note on acidity in (4 p.).]

[1] Paper No. 194 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

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Carbonates and bicarbonates

The amount of carbonates and bicarbonates in the extracts follows the tendencies of the reaction, i.e. whenever leaching was facilitated a great part of these substances left the soil. The persistence of the carbonates for a longer period than in the first series may be ascribed to the variation in procedure, as mentioned. The addition of sulfur to the surface soil was not nearly so efficient in decomposing the carbonates as the method of incorporating the

TABLE 1

Treatment of alkali soils, second series

LABORATORY NUMBER	TREATMENT
1	None
2	2000 pounds sulfur applied to surface 4 inches
3	2000 pounds sulfur mixed with bulk of soil
4	4000 pounds sulfur applied to surface 4 inches
5	4000 pounds sulfur mixed with bulk of soil
6	6000 pounds sulfur applied to surface 4 inches
7	6000 pounds sulfur mixed with bulk of soil
8	4000 pounds c.p. alum

TABLE 2

Analyses of leachings after 15 days' incubation; 2d series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH PER POT	C AS CO_3	C AS HCO_3	Cl	Ca	K	S AS SULFATES	REACTION
	cc.	*p.p.m.**	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*pH*
1	91	11.9	386	1639	5.3	388	567	9.4
2	110	23.4	551	2356	3.8	1111	664	9.2
3	87	26.5	546	2650	2.2	673	597	9.4
4	150	25.3	601	2712	2.2	448	344	9.2
5	110	14.6	485	2352	5.3	543	566	9.4
6	87	32.3	556	2700	2.6	413	661	9.5
7	125	15.6	515	2639	3.8	281	651	9.4
8	97	3.6	230	2756	7.3	494	788	9.0

* Parts per million of air-dry soil.

sulfur with the bulk of the soil. It is unquestionable that mixing the sulfur with the bulk of the soil was the better method. It is questionable, however, whether such a practice may be carried out in the field.

The procedure followed in this series of experiments for the extracts gives a better index to the relation between the total carbonates and bicarbonates and those leached than in the first series. The bicarbonates in the leachings fluctuate between 40 and 60 per cent of the total, if the total is taken as the sum of the bicarbonates from the leachings and the extracts on one and the same pot. Attention is called to the fact that such a total does not correspond

TABLE 3

Analyses of leachings after 30 days' incubation; 2d series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH PER POT	C AS CO₃	C AS HCO₃	Cl	Ca	K	Na	S AS SULFATES	REACTION
	cc.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m	pH
1	165	42.0	733	3194	16.2	118	263	693	9.4
2	191	18.7	569	3038	58.8	105	255	839	9.2
3	153	4.7	278	2696	30.7	138	235	824	8.9
4	224	17.0	538	3398	16.2	334	140	953	9.2
5	182	2.1	184	2874	10.2	116	202	1030	8.6
6	212	11.0	459	3286	24.3	137		951	8.8
7	165	1.1	150	2739	24.3	86	241	1020	8.2
8	201	9.3	466	3426	22.6	195	223	988	8.6

TABLE 4

Analysis of extracts of leached cultures after 30 days' incubation; 2d series

LABORATORY NUMBER OF TREATMENT	C AS CO₃	C AS HCO₃	Cl	Ca	S AS SULFATES	REACTION
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	pH
2	29.4	314.0	2600	100	1017	8.2
3	29.4	295.0	2600	90	1061	8.4
4	24.5	295.0	1600	100	981	8.2
5	Trace	310.0	2900	100	1247	8.2
6	0.0	260.6	1600	90	1094	8.0
7	0.0	260.6	2200	100	1247	8.0
8	49.0	353.8	1300	80	686	8.6

TABLE 5

Analyses of leachings after 75 days' incubation; 2d series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH PER POT	C AS CO₃	C AS HCO₃	Cl	Ca	Mg	K	Na	S AS SULFATES
	cc.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
1	105	16.5	422	2089.8	6.8	5.6	184.3	1996	406.7
2	205	7.2	371	3176.8	2.7	15.8	209.2	3165	918.6
3	157	1.6	162	2547.7	6.91	28.4	205.6	2668	852.0
4	252	7.4	389	3169.0	4.70	22.4	206.8	3251	996.0
5	190	1.0	145	2732.7	13.08	44.6	200.9	2940	1023.8
6	272	3.9	295	3215.1	9.27	37.2	189.0	3513	1071.0
7	237	0.9	156	3198.0	15.36	67.0	231.6	3329	1233.0
8	225	10.26	460	3421.7	24.06	11.1	283.6	3370	950.9
2*	240	11.3	520	3215.0	3.9	22.2	170.2	3528	1000.2
3*	245	2.8	243	3352.8	12.46	57.7	186.7	3518	942.3

* Means that after 30 days 2000 pounds more sulfur was added to the surface 4 inches of soil, making a total of 4000 pounds.

to the total obtained when the culture was extracted before leaching; invariably it is higher.   The difference must be ascribed to the formation of soluble carbonates during the process of drying from the time of leaching to the time of extraction, usually about 10 days.   The alum cultures show a very slight decrease in the total carbonates and bicarbonates.   Not all of the carbonates disappeared.

TABLE 6

Analyses of extracts of leached cultures after 75 days' incubation; 2d series

LABORATORY NUMBER OF TREATMENT	C AS CO₂	C AS HCO₃	Cl	Ca	Mg	K	Na	S AS SULFATES	REACTION
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*pH*
1	49.00	314.7	1700	180.45	82.95	273.45	3477.09	363.7	9.4
2	74.50	270.4	800	180.45	91.69	209.11	2510.38	284.4	9.0
3	19.6	304.9	900	170.42	65.49	199.45	2973.96	306.3	8.6
4	Trace	186.8	800	220.55	89.50	212.32	5190.95†	464.9	8.4
5	00	162.3	748	210.52	80.77	218.76	2857.20	448.5	8.2
6	00	147.5	600	260.65	52.39	199.45	1793.76	470.4	8.2
7	00	98.3	748	360.90	111.33	186.59	1142.51	711.04	8.0
8	39.2	324.5	600	110.27	78.59	199.45	4940.96†	136.7	9.2
2*	Trace	181.93	800	280.70	72.04	218.76	1378.01	582.5	8.4
3*	00	157.3	1100	280.70	69.86	176.94	1755.58	801.30	8.2

* Cultures were leached after 30 days and 2000 pounds of sulfur were incorporated in the surface four inches of soil making a total of 4000 pounds.

† These results cannot be explained; there must have been an error in the determination.

TABLE 7

Analyses of leachings after 140 days' incubation; 2d series

LABORATORY NUMBER OF TREATMENT	AMOUNT LEACHED THROUGH PER POT	C AS CO₂	C AS HCO₃	Cl	Ca	Mg	K	Na	S AS SULFATES	REACTION
	cc.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*pH*
1	150	26.4	498	3073	5.5	2.9	119.171	2863.69	551	9.4
2	257	3.0	240	3391	52.8	20.5	108.509	3708.60	845	8.5
3	244	1.2	162	3293	103.9	37.9	103.091	3357.08	1028	8.3
4	237	1.6	217	3165	71.4	29.9	112.126	3649.95	974	8.6
5	255	0.0	143	3033	114.7	57.2	105.720	3300.19	1043	8.2
6	260	0.7	204	3212	95.0	47.7	105.332	3671.65	1102	8.4
7	237	0.0	95	2896	103.5	77.0	140.424	3340.95	964	7.8
8	225	7.8	373	3589	18.7	6.2	112.563	3642.85	873	9.2
2*	245	0.7	180	3316	66.7	41.3	76.013	3746.44	1024	8.2
3*	233	0.0	71	2397	77.6	45.7			941	8.0
2†	255	1.6	211	3232	56.3	22.9	94.041		991	8.6
3†	250	1.2	155	3008	99.6	36.3			964	8.4

* Means that 2000 pounds of sulfur was added after 30 days without leaching making a total of 4000 pounds of sulfur.   Peat at the rate of 5 tons per acre was also added after 30 days.   These were leached only after 140 days.

† Peat was added to these cultures after 30 days.

TABLE 8

Analyses of extracts of leached cultures after 140 days' incubation; 2d series

LABORA-TORY NUMBER OF TREAT-MENT	C AS CO₂	C AS HCO₃	Cl	Ca	Mg	Fe	K	Na	S AS SUL-FATES	REAC-TION
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*pH*
1	53.9	329.4	1300	120.3	93.8	670.8	318.4	1715.8	382.8	9.0
2	4.9	265.5	650	154.3	89.5	559.0	276.6	1008.4	328.1	8.2
3	4.9	265.5	650	160.4	82.9	614.9	260.5	1345.2	339.1	8.2
4	0.0	177.0	700	210.6	93.8	391.3	225.1	1429.9	508.6	8.0
5	0.0	118.0	850	250.5	74.2	279.5	225.1	1689.5	563.3	7.8
6	0.0	132.7	750	270.5	78.5	335.4	221.9	1738.0	607.1	7.8
7	0.0	78.6	750	681.0	69.8	167.7	270.2	1435.8	1080.2	7.4
8	29.4	341.7	650	130.5	137.5	614.9	295.9	1166.0	185.9	8.8

TABLE 9

Analyses of leachings after 190 days' incubation; 2d series

LABORA-TORY NUMBER OF TREAT-MENT	AMOUNT LEACHED THROUGH PER POT	C AS CO₂	C AS HCO₃	Cl	Ca	Mg	K	Na	S AS SUL-FATES	REAC-TION
	cc.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*pH*
1	60†	12.1	249	1681	2.6	3.8	79.4	1455	337.6	9.4
2	252	0.4	240	3252	66.3	28.3	113.5	3623	1043.0	8.2
3	225	....	76	3073	90.2	36.0	121.9	3282	1022.0	8.2
4	215	....	137	3073	73.0	51.5	105.0	3425	1085.0	8.2
5	270	....	132	3362	95.6	73.6	105.0	3919	1311.0	8.0
6	250	....	125	2990	86.6	65.9	89.1	3367	1082.0	8.0
7	220	....	78	3141	98.1		102.1	3479	1218.0	7.2
8	125†	0.7	211	2962	17.2	15.6	113.5	3037	768.7	8.8
2*	220	....	91	331	25.2		22.7	598	307.4	8.2
3*	215	....	48	331	59.2		56.7	625	358.7	7.6

* These were leached after 140 days, at which time an addition of 2000 pounds of sulfur and peat at the rate of 5 tons per acre were added.

† These became water logged after 48 hours. No. 1, therefore, received only 285 cc. and No. 8, 315 cc. All others received 400 cc. and leached through in 20–24 hours.

TABLE 10

Analyses of extracts of unleached cultures after 190 days' incubation; 2d series

LABORATORY NUMBER OF TREATMENT	C AS CO₂	C AS HCO₃	Cl	Mg	K	Na	S AS SULFATES
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1	31.36	420.89	4200	207.39	180.152	5215.087	820.44
3	0.0	153.10	4100	130.98	102.944	5194.33	1490.47
4	0.0	125.87	4100	98.235	93.293	4965.53	1679.17
6	0.0	116.04	3900	141.89	70.774	4982.42	1845.99
7	0.0	66.87	4200	148.44	83.642	5130.13	2392.95
8	7.84	277.32	4000	87.32	119.029	4474.14	1080.25

Chlorides

The cultures of the 30-day incubation period show an abnormally high chlorine content. It cannot be explained except on the basis of some error in the analyses detected too late to be checked up. The other cultures show that there are about 4000 parts per million of chlorine in this particular soil. These experiments substantiate the conclusions reached, in the third paper of this series (4) in regard to the chlorine in alkali soils: it is easily leached out.

Calcium

Not much more may be said about the calcium data in this series than what has been said about it the first series. The increase in the calcium of the sulfur-treated cultures undoubtedly points to the presence of large amounts of this

TABLE 11

*Analyses of second leachings after 335 days of cultures leached for the first time after 190 days' incubation; 2d series**

LABORATORY NUMBER OF TREATMENT	C AS CO_3	C AS HCO_3	Cl	Ca	Mg	K	Na	S AS SULFATES	REAC- TION
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	pH
2	1.84	24.6	383.0	25.3	16.0	27.0	632.3	326.8	8.8
3	1.46	20.5	617.2	28.9	11.6	34.8	948.4	348.4	8.6
4	0.97	12.8	507.0	76.0	61.3	36.9	824.0	470.6	8.4
5	0.0	6.12	388.5	88.4	29.5	33.3	658.1	376.2	8.0
6	Trace	12.7	647.5	182.7	142.5	70.2	1233.3	786.2	8.2
7	0.0	2.00	542.8	92.5	64.8	44.0	832.9	559.5	6.4
2†	0.0	5.58	330.6	93.1	47.5	31.9	644.53	460.6	8.0

* No leachings could be obtained from the untreated cultures. Not a drop leached through even after being in contact with the water for 10 days.

† This culture was treated originally with 2000 pounds of sulfur. After 140 days it was leached and to it 2000 pounds more sulfur was added. Leached again after 335 days.

cation in the zeolitic portion of this soil. The data on the calcium in table 11 where analyses of the second leachings are reported show that more calcium has come out from the zeolites. One other point has to be kept in mind in interpreting the calcium figures. On account of the preponderance of the sulfate ion a great deal of the calcium combines with it, forming gypsum. The extracts, therefore, do not show the true amount of calcium replaced. An analysis of the zeolitic cations capable of replacement will give the true value. This is being investigated and indications are on hand proving the truth of the assumption.

Magnesium

There is not much soluble magnesium in this particular soil, neither is there any zeolitic magnesium capable of replacement. From 15 to 30 per cent of the total is leached out.

Sodium

Outside of the few discrepancies indicated in the tables, the data on the sodium shows that the soil under investigation has not much zeolitic sodium to be replaced. There is some increase in the sodium content of the treated cultures. If the sodium had been in preponderance, then the calcium with its higher coefficient of absorption would not have been replaced last. The data of the second series of experiments confirm the postulate made in the third paper (4), namely, that this soil is not a purely sodium alkali soil. The presence of large amounts of sodium in solution points to the genesis of this alkali soil, namely that it is either in the process of desalinizing or *more likely in the process of formation*. Table 11 gives the data on cultures which have been leached once after 190 days and then again after 335 days. If there were zeolitic sodium it would have shown up in these second leachings. There are, however, only slight indications of this nature.

Potassium

The conclusions reached in the first series of experiments, notwithstanding the errors due to the pots, have been fully substantiated by this second series.

Sulfur

The extracts and the leachings do not show the true amount of the sulfur oxidized, since appreciable amounts of the sulfates combine with the calcium replaced, forming gypsum. That in some cases all of the sulfur has been oxidized may be inferred from the data on the reaction and carbonates in table 11. If sulfur were there the reaction could not have gone back to more alkalinity and no soluble carbonates could exist. The figures in table 11 are instructive in another way; they show that only 6000 pounds of sulfur is capable of bringing the reaction towards slight acidity and that 4000 pounds of sulfur is sufficient to keep down the soluble carbonates. These facts shall corroborate the studies on the zeolitic cations capable of replacement and a correlation of the two shall give a pretty close answer to the question of how much sulfur is necessary to apply to this particular soil to keep a favorable reaction for plant growth and at the same time keep away the soluble carbonates.

GENERAL DISCUSSION ON DIFFERENT AMELIORATING AGENTS

The studies on the California alkali soil as revealed in the analytical data of the two series of experiments presented in the previous papers and in this paper suggest some specific ideas on the subject.

The treatment of any black alkali soil must be guided by the principles mentioned (3, p. 18). To accomplish the favorable effects as a result of the application of these principles the proper agent in reclaiming the black alkali soils is of prime importance. The three agents discussed are gypsum, alum, and sulfur. A summary of their merits as ameliorating agents may not be out of place.

Gypsum

The initial step in treating black alkali soils as outlined by the authors is to coagulate the colloids. This brings about a marked improvement in the physical condition of the soil, makes it pervious to water and thus allows efficient leaching. Because they did not consider the factor of colloids, the earlier investigators and even some recent ones have recommended gypsum under all conditions. From the discussion presented in this series of papers by the authors, it should be clear that gypsum on account of its slow solubility cannot be reckoned as an efficient coagulant.

The second step in any rational method of treating black alkali soils is the replacing of the zeolitic sodium or any other cation. Gypsum allows only few calcium ions to be active in the replacement process because of its slight solubility. The low concentration of calcium ions is rapidly overwhelmed by the increasing concentration of the sodium ions; under such a condition no more calcium may enter the zeolitic portion even though it has a higher coefficient of absorption for reasons pointed out (3, 4). If, upon leaching, the sodium compounds come back from the lower horizons to the surface horizons, then the newly accumulated excess of sodium in the soil solution will replace the few calcium ions from the gypsum which entered the zeolitic portion of the soil; the calcium will then combine with whatever anion the sodium was in combination as it came from the lower horizons. In the case of sodium chloride, the toxic calcium chloride is formed. Otherwise gypsum is formed again and equilibrium is reached in the system. At this point, if carbonates are present, there is the possibility of forming soda.

The cycle thus described fully supports the theory of Gedroiz on the process of black alkali soil formation. The only exception where the theory of Dominicis, which does not require the presence of carbonates (3, p. 17), may be upheld, is when some hydrogen ions from water enter in the replacement process leaving behind the hydroxyl ions; these unite with the Na ions forming NaOH, which absorbs CO_2 and forms soda.

The third step in this process is to create a favorable reaction for plant growth. Gypsum may not be relied upon to reduce the alkalinity, since the products of the reaction are not of an acid nature; inasmuch as the soluble carbonates are converted into insoluble carbonates, some reduction of alkalinity will take place. We must agree, however, that the driving force of the reaction towards the insoluble carbonates is greater than in the reverse direction, something which is not at all always probable. The work of Kelley and Thomas (5) substantiate the above conjectures.

Alum

The use of alum to accomplish the first step mentioned has been suggested by Scofield [see reference in earlier paper (3, p. 30)]. An application of alum brings about a favorable condition for leaching since the trivalent aluminum is an excellent colloid coagulant.

In reference to the replacement capacity of alum it is interesting to note that only the potassium cation seems to be able to serve as a replacing agent; the aluminum apparently does not take part in this reaction. For this reason the usefulness of alum as an ameliorating agent ceases with its coagulation reactions. There may be conditions, however, which will justify the use of alum (the practicability from standpoint of cost is not considered here) and these may be as follows:

1. In an alkali soil not saturated with sodium in its zeolitic portion, but in which the sodium carbonate is beginning to show. Cases of that sort may be found in black alkali soil region in process of formation, *the probable condition of the California soil under investigation.*

2. In such a soil leaching alone could accomplish the task of removing the excessive soluble salts and the alum treatment would be sufficient if means could be provided to prevent the sodium from the lower horizons from coming to the surface. The maintaining of such a condition is possible by means of a good drainage system, if such may be constructed conveniently.

As far as the third step (reaction) is concerned, the alum as shown by the studies in these papers can reduce the alkalinity only inasmuch as the alum carries free acid with it. The amount of soluble carbonates, as may be seen from the tables, has changed but little. Thus the use of alum as a remedy to change the inherent characters of black alkali soil cannot be advised, and its merits are limited.

Sulfur

In the form of commercial flour, sulfur does not react to any extent and therefore may be disregarded as a coagulant of colloids. Its use as an effective coagulating agent is based on the biological oxidation with the formation of sulfuric acid as an end product. After fourteen days, as shown previously (4), the colloids have been coagulated. It is interesting to note that the behavior of sulfuric acid in respect to coagulating power differs in the alkali soil extracts and alkali soil itself; in the soil its coagulating power is quite marked, while in the extracts it is insignificant. The effectiveness in the soil may be attributed to compounds other than the sulfuric acid itself; these compounds in combination with the sulfuric acid are probably responsible for the high coagulating powers.
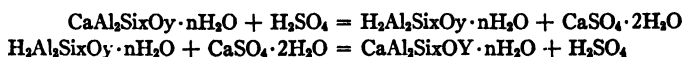
In regard to the replacing power of the sulfur oxidation products not much may be added in the summary. The hydrogen ions tend towards the formation of an acid soil replacing all the cations in the zeolites with hydrogen. In black alkali soils with sodium saturated zeolites the surest and quickest method would be the replacement by hydrogen. Any sodium from the compounds, which are bound to come from the lower horizons or from the irrigation waters, is prevented from entering the zeolites on account of the high coefficient of adsorption of the hydrogen ions. Furthermore, it would be advantageous to use lime after the sodium compounds have been replaced and the soil has been leached. The calcium ions would enter the zeolitic portion forming calcium

zeolites, and as long as an excess of sodium could be prevented from invading the soil again such a procedure would bring the soil to an ideal physical and chemical condition.

Sulfur oxidation prevents the formation of any soluble carbonates; the hydrogen-ion concentration of the extract may be kept at a level which should not be injurious for plant growth. If the soil is a calcium-sodium alkali then the products of sulfur oxidation replace the calcium which upon entering the soil solution forms gypsum; eventually the calcium ion would tend to go back into the zeolite. In a calcium alkali soil the amount of sulfur necessary will be guided by the leaching capacity of the soil. It is understood that steps are to be taken to prevent other alkali forming substances from rising to the surface. As a rule, however, sodium accompanies the calcium and under such conditions it is important to have an excess of sulfur to prevent the formation of soda.

<div align="center">PRACTICAL CONCLUSIONS</div>

The soil under investigation has some soda and also some sodium in the zeolitic portion. For the best results the following reasoning may serve as a guide in deciding upon the time of leaching. When the colloids have been coagulated, the carbonates begin to disappear; some go off as CO_2, some are converted into bicarbonates, some CO_2 is utilized by the autotrophic microbial flora. The reactions with the carbonates probably take place first, since they are solution reactions. They are followed by replacement reactions. From the nature of the cations it is expected that sodium shall come out first followed by calcium. In making frequent determinations, the point at which all or most of the sodium has been replaced may be detected; only then leaching should be resorted to. The sulfur oxidation following leaching will supply the hydrogen ions for the replacement of the calcium, which as mentioned forms gypsum. After all the sulfur has been oxidized and the supply of hydrogen ions has been exhausted the reverse reactions will take place as shown in the following equations:

$$CaAl_2SixOy \cdot nH_2O + H_2SO_4 = H_2Al_2SixOy \cdot nH_2O + CaSO_4 \cdot 2H_2O$$
$$H_2Al_2SixOy \cdot nH_2O + CaSO_4 \cdot 2H_2O = CaAl_2SixOY \cdot nH_2O + H_2SO_4$$

No definite amount of sulfur may be recommended; a quantitative determination of the replaceable cations, as indicated previously, will tell the story. It seems as if 4000 to 6000 pounds of sulfur was sufficient under the conditions of these experiments.

The combination effects of sulfur and alum in ameliorating the physical condition of the soil bring forth the possibility of the use of these two ameliorating agents in treating alkali soils. The advantage would be that the alum would immediately coagulate the colloids and thus the hydrogen ions from the sulfuric acid would be utilized for the replacement of the sodium. Such a procedure is apt to shorten the period of reclamation. Further studies in this

direction would probably show more concrete possibilities of these two ameliorating agents.

The use of organic substances such as peat or large amounts of manure are effective inasmuch as they serve as buffers and constituents to be reacted upon by the soda. They have not, however, any cations capable of replacing the noxious cations of the zeolitic portion of the soil. Their effectiveness is, therefore, only temporary. One thing, however, that these organic substances introduce, is some plant food which a number of alkali soils lack.

Fertilizer application

The soil under investigation, as pointed out, is very poor in nitrogen. It has not very much of phosphates either. These soils after treatment would respond to fertilizers. The most logical inorganic nitrogen source would be ammonium sulfate. It is possible that the NH_4 ions become fixed in the zeolitic portion only to be replaced later by the calcium ions of the gypsum. Whether nitrification of the ammonium is possible while it is in an adsorbed condition in the zeolitic portion is of course problematic; it probably would be nitrified as it is replaced and from this point of view it would be of an advantage since none would be leached out. Ammonia determinations at the various periods of incubation would tell the story. This subject has not been investigated.

From the nature of the alkali soils it would be logical to use calcium nitrate, having the calcium as one ion that enters the zeolitic portion. After leaching, an application of lime would be advantageous augmenting the store of calcium for replacement. Whenever alum alone may accomplish the ameliorating effects, an application of gypsum would be the better source of calcium.

BIOLOGICAL EFFECTS

The study of any soil problem is incomplete, unless all of the phases of soil fertility are looked into. It has long been recognized that the biological structure of the soil plays an important rôle in soil processes and in the reactions accompanying them. No definite function or group of functions have been as yet found to serve as a guide to get a clear idea of the existing relationships between the biological structure of the soil and soil fertility. The increase in numbers of bacteria, one of the earliest phases investigated and recognized, has often served as an excellent indication of the probable condition of the soil.

It has been suggested by Barnes and Ali (1) that the salts present in alkali soil do not exert any toxic effect on the plant. The danger point in alkali soil is reached when the osmotic pressure of the saline solution becomes equal to that of the cell sap. This happens irrespective of the nature of the salt provided it possesses no toxic properties. Such salts as sulfates and chlorides of sodium or calcium exhibit no toxic properties to plant protoplasm. Even

Na_2CO_3 cannot be said to be toxic though it is known that it shows evidence of caustic action on the stems of the plants. Whether the caustic effect is produced on dead or living tissue is not known. They conclude therefore that CO_2 formation, nitrification and nitrogen fixation might be used to measure the crop producing power of alkali soils. These views are interesting and deserve more attention; their conclusions, however, seem to be of little value, since the question of indications for the productivity in alkali soils is not at all troublesome.

The condition of the black alkali soil investigated is such that no green plants are capable of carrying on their active life processes. Still the bacteria exist and undoubtedly function.

Bacterial numbers

Table 12 gives the number of bacteria in alkali soils at the various incubation periods with the different treatments under leached and unleached conditions.

It is of interest to note that there is practically no increase in bacterial numbers after 60 days of incubation. The data in general do not seem to substantiate the supposition of Barnes and Ali, since even without leaching an increase in bacterial numbers after 95 days incubation with the high sulfur applications may be noted. It is very probable that if toxic effects are responsible for the low count of bacteria then the increase of calcium due to the replacement process is by the force of its antagonism responsible for the increase in number; the decrease in soluble carbonates will also tend to work in that direction. The decrease in numbers after 140 days may be explained on the basis of increased concentration of salts due to the sulfur oxidation. Vegetation experiments showed somewhat similar results as pointed out presently. It is worth while to record that in no case has the alum treatment caused an appreciable increase in the bacterial numbers; neither has the peat. This again points to the low efficiency of these substances as ameliorating agents of alkali soil conditions.

Nitrification

Alkali soil cultures variously treated and leached at the various incubation periods were air-dried, 100-gm. portions were placed in tumblers and to each one 25 mgm. of nitrogen in the form of ammonium sulfate or dried blood was added. Table 13 gives the data on the nitrate nitrogen found after 46 days of incubation.

The results are conflicting and no conclusions may be drawn. A great deal of the inconsistent results must be ascribed to the method used in determining nitrate nitrogen. It is known that chlorides interfere with the determination of nitrates and they have to be precipitated with silver sulfate. Even then it was found that in many cases some nitrates could not be recovered and in some cases the results were too high. The data on the unleached cultures give an idea of the amount of nitrates present in this alkali soil.

TABLE 12

Influence of treatment on bacterial numbers in alkali soil

LABORATORY NUMBER OF TREATMENT	TREATMENT	BACTERIA PER GRAM OF SOIL AFTER				
		14 days*	60 days†	95 days†	108 days‡	140 days†
		hundred thousands	*hundred thousands*	*hundred thousands*	*hundred thousands*	*hundred thousands*
1	None......................	5.94	4.92	5.44	4.41	4.92
2	4000 pounds sulfur...........	6.40	4.40	4.85	9.92	5.61
3	4000 pounds sulfur + 5 tons peat......................	7.41	4.96	5.81	17.07	5.78
4	6000 pounds sulfur...........	4.45	5.97	13.20	32.05	6.33
5	6000 pounds sulfur + 5 tons peat......................	6.40	5.80	23.00	69.33	12.52
6	2000 pounds sulfur...........	6.07	4.73	4.55	6.9	5.08
7	2000 pounds sulfur + 5 tons peat......................	4.16	4.71	4.96	6.2	5.41
8	4000 pounds c.p. alum + 5 tons peat......................	4.63	4.91	5.41	4.28	5.63
9	4000 pounds c.p. alum + 2000 pounds sulfur.............	5.96	4 04	4.36	5.4	5.60
11	5 tons peat.................		5.80	4.1	6.1	5.36

* Bacterial numbers determined on soils after leaching.

† Unleached.

‡ These were leached twice; first after 14 days.

TABLE 13

Nitrate nitrogen after 46 days' incubation in alkali soils variously treated for various incubation periods

LABORATORY NUMBER OF TREATMENT	INCUBATION PERIOD OF TREATED SOILS								
	Dried blood					$(NH_4)_2 SO_4$			
	15 days	30 days	75 days	140 days	190 days*	15 days	30 days	75 days	140 days
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1	46.2		21.95	23.1	160.0	62.4		39.2	31.2
2	66.6	49.0	39.2	25.5		54.0	19.6	14.7	19.6
3	62.7	27.0	23.1	32.3	224.0	54.0	23.1	21.5	27.0
4	69.8	29.4	23.1	10.2	192.0	62.4	12.7	14.6	86.2
5	66.6	15.7	86.2	23.1		54.0	8.8	39.2	13.5
6	74.5	24.5	58.8	27.4	208.0	54.0	8.8	21.6	10.8
7	51.0	11.7	21.5	23.1	160.0	54.0	4.6	7.8	13.5
8	53.0	4.9	35.3	39.2	192.0	62.4	10.8	14.6	25.5

*Nitrogen as nitrates on unleached cultures.

Vegetation experiments

The soil under investigation is bare of vegetation. Whether toxicity, reaction or osmotic concentration is responsible for the practical sterility of the soil as far as green plants is concerned matters little at the present moment;

it is probable that a combination of these three factors is responsible for the results. Wherever thorough leaching was possible vegetation could be established. The alum treatment was efficient therefore in the beginning. However, if the alum treatment was not followed immediately with leaching there was no hope of obtaining a stand of any kind of a crop. This was evident from the first series of experiments. In the second series a more accurate account may be given since in this series some of the errors, like absorption by walls of pots, were eliminated. All the records as given in table 14 and plate 1 are on leached soils, except that of 190 days.

It will be noted from table 14 that the barley made growth even on the untreated cultures (no. 1) after 15 and 30 days. The reason for such a behavior is that at this period the soils were not as compact and allowed leaching. However, in the later periods of incubation the soils became compacted pre-

TABLE 14

*Record of barley crop grown in pots of variously treated alkali soils after various incubation periods**

LABORATORY NUMBER OF TREATMENT	DRY WEIGHT OF CROP			
	15 days	30 days	75 days	190 days†
	gm.	*gm.*	*gm.*	*gm.*
1	0.136	0.160	0.000	0.000
2	0.413	0.525	0.507	0.155
3	0.283	0.394	0.462	0.124
4	0.299	0.344	0.547	0.140
5	0.314	0.456	0.464	0.151
6	0.365	0.251	0.539	0.099
7	0.129	0.420	0.473	0.089
8	0.058	0.138	0.000	0.000

* The barley was attacked by mildew and the crop had to be harvested before maturity.
† This lot was planted before leaching. The same pots were leached and planted to millet. Plate 1 gives the results.

venting the leaching of the untreated cultures. Then the noxious features of the alkali soils became apparent: the barley barely germinated, but made no growth. The figures on the 190 day cultures are interesting. They show that even without leaching some growth may be obtained on treated soil although not as goos as when leached. These figures bear out the data on bacterial numbers. It is undoubtedly true that the neutralization of the soda and the bringing into solution of calcium ions which antagonize other toxic elements, had their influence. Still it is apparent that the concentration of the salts prevented better growth; especially is this evident from cultures 6 and 7, the highest sulfur application.

After the barley was harvested millet was planted. Plate 1 is a photograph of the 190-day culture where barley was grown before leaching, leached after that and planted to millet. The 190-day set was selected as typical and the photograph is self-explanatory.

CONCLUSION

This series of papers reporting the work with alkali soil should be looked upon as an attempt to bring before the investigators in this important field of research a clear picture of the problem as revealed by the most recent theories on the subject, especially that of Gedroiz. The data presented in the light of these theories seem to give a theoretical working basis; the practical aspect of the problem will undoubtedly force a modification of the steps involved; the principles outlined, however, seem to be sound.

METHODS OF ANALYSIS

Whenever possible, the official methods were used and there is no necessity in pointing out the details. The extracts were prepared by mixing 50 gm. of soil with 500 cc. of distilled water. The mixture was shaken every ten minutes during the day, left over night, decanted, centrifuged for 1.5 hours and then filtered through plaited filter. The first 100 cc. were discarded, allowing the filter to saturate with the solution.

The hydrogen-ion concentration of the leachings or extracts was determined colorimetrically by the Clark and Lubs method as outlined in Clark (2). Wherever the colors failed to give a good reading the potentiometer was used.

In making bacterial counts, 8 to 10 plates were used for each culture with a synthetic medium consisting of the regular mineral salts with 1 per cent dextrose as the source of carbon and egg-albumin .05 per cent, as the source of nitrogen. The reaction of the medium was adjusted to pH 6.8–7.0.

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PLATE 1

Numbers indicate treatment as outlined in table 1. Pots 2, and 3, have been leached after 140 days and 2000 pounds more sulfur added to them.

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THE DETERMINATION OF AMMONIA IN SOIL

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Easily available nitrogen, particularly in the form of ammonia and nitrates, is one of the factors which most energetically accelerate the biological processes in the soil, e.g., the fermentation of cellulose (4). For soil biological research, therefore, it is of great importance to have methods by which these nitrogen compounds can be accurately determined. As for the nitrates, we have the exact phenol-disulfonic method. For ammonia, many methods have been proposed but some results obtained in this laboratory have indicated that the soil ammonia problem requires a reëxamination.

INTRODUCTION

Most of the soil nitrogen has its origin in the form of highly complex protein compounds. Under natural conditions these are decomposed very slowly and thereby amino acids and acid amids are gradually formed, which in their turn are hydrolyzed with the formation of ammonia. The ammonia nitrogen thus produced undergoes the further changes of the nitrogen cycle. One of the two big difficulties which arise when soil ammonia is to be determined is to establish this free ammonia without splitting off ammonia from the protein compounds or the intermediary compounds by the necessary chemical or physical operations.

Boussingault was probably the first to determine ammonia in soil. In order to avoid such hydrolysis he boiled the sample with the weak alkali MgO in water, fixed the liberated ammonia in sulfuric acid of known strength, and then determined the ammonia content by titration. However, it was found, especially with soils rich in humus, that the fresh distillate after continued treatment in this way reacts alkaline and that consequently ammonia is formed during the process. To avoid a quite arbitrary endpoint new methods were worked out. Schlösing modified the method of Boussingault in that he distilled a hydrochloric acid extract of the soil with MgO. Grandeau (11) as well as Baumann (5, 6) tested Schlösing's method and found it reliable. That nitrogen compounds can also be decomposed in Schlösing's method is indicated by the work of Berthelot and André (7). The azotometric method of Knop and Wolf (14) by which the soil is mixed with a solution of NaOH and NaOBr, whereupon the ammonia nitrogen is liberated as free nitrogen was rejected by Baumann because it gave ammonia figures to soils which were

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free from ammonia according to Schlösing's method. Furthermore, strange contractions took place with the gasometric method which were difficult to eliminate. Valmari (25) tried to extract the ammonia with the neutral electrolytes NaCl, CaCl₂ and CaCO₃, after which the ammonia was determined on an aliquot of the filtered extract by distillation with MgO. From his results Valmari concluded that solutions of neutral electrolytes even in low concentrations remove all the soil ammonia, and that generally 0.1 N NaCl in the extracting ratio, that is, the ratio between soil and liquid, 1:40 or 1:20 will be suitable for peat soils, 0.2 N NaCl in the ratio 1:10 for peat loam soils, and 0.5 N NaCl in the ratio 1:2 for mineral soils.

In the study of all the related methods, they were controlled by continuing the process for such a period as was thought sufficient for complete ammonia liberation and by making blanks on organic nitrogen compounds such as amino acids, acid amids, and other nitrogenous organic compounds. In determining the efficiency of various methods, no one, it seems, with the exception of Knop and Wolf (14) tried to recover from the soil ammonia previously added in known amount in the form of ammonium salts.

During the last decennium control investigations of this kind have been taken up again by Potter and Snyder (21), McBeth (19), and others, who found that soils retain ammonia nitrogen supplied in the form of ammonia or ammonium salts so firmly that it cannot be recovered quantitatively by any one of the usual methods for the determination of ammonia in soil.

Since added ammonia could not be recovered by the old methods for the determination of soil ammonia, the problem has been treated again by several investigators, who have worked out new methods. The purpose of this work was to determine whether these new methods are generally applicable and also to find out how far certain factors influence the ammonia-fixing power of the soil. Then, guided by these results, it was hoped to find a new way to solve the problem.

It appears from the foregoing that the properties such a method should possess, besides being rapid and simple, are;

1. The ammonia nitrogen of the soil should be liberated quantitatively and none should be produced from organic nitrogen compounds during the work, even after the addition of such compounds.

2. In the case of a soil to which ammonia nitrogen has been added, the method must be able to recover this quantitatively together with the soil ammonia nitrogen.

That the fulfillment of point 2 is not a sufficient condition is illustrated by the following example from an investigation of this kind on manure (4). Boussingault's method as well as that of Baragiola and Schuppli (1) accounted quantitatively for added ammonia nitrogen, but the former method gave the higher total yield, due to liberation of more ammonia from the control. Thus Boussingault's method gave incorrect results for the material in question, but to determine whether the latter method really is correct it must be tested according to point 1.

The second condition being essential, the work first related was an attempt to find out how the different methods behaved with reference to soils to which ammonia nitrogen was added. Some of the results presented here have already been published (2, 3), but for the sake of completeness they are included. The following soils were used in the experiments:

		pH
Soil I.	Silt loam soil from Experimentalfältet	5.7
Soil II.	Heavy clay soil from Experimentalfältet	7.1
Soil III.	Peat loam soil from Experimentalfältet	5.3
Soil IV.	Sandy soil from Risbyn, Avesta	5.0
Soil V.	Sandy soil from Experimentalfältet	6.1
Soil VI.	Loam soil from Experimentalfältet	5.5
Soil VII.	Peat loam soil from Vassbo, Ornäs	5.4

BOUSSINGAULT'S METHOD

McBeth found that the methods of Boussingault and Schlösing were very nearly of the same worth in the recovery of added ammonia. For the determinations of soil ammonia which have previously been made in this laboratory only the former of these methods were used. As a rule, those investigations had reference to soils relatively poor in humus for which, according to König (15), the Boussingault method gives approximately correct values. For the estimation of our earlier results it was, therefore, of interest to examine to what extent added ammonia nitrogen could be liberated from these soils by the Boussingault method. The determinations were made by heating 50 gm. of soil with about 5 gm. of MgO and 500 cc. of distilled water. A piece of bees' wax was added otprevent foaming. The liberated ammonia was caught in 0.1 N H_2SO_4. Three hundred cubic centimeters of distillate was taken since a preliminary experiment with soil II had shown that the part of the added ammonia which was removable was obtained in this volume. The distillates were boiled for a few minutes, after which they were titrated after cooling with 0.1 N NaOH, cochineal being used as the indicator. In those cases where the soil was supplied with ammonia nitrogen this was always added in the form of $(NH_4)_2SO_4$ solution in a volume of 25 cc. per 50 gm. of soil. This volume of liquid always proved to be sufficient to wet the whole sample thoroughly. After repeated shaking the mixture was allowed to stand 1 hour before examination.

A block of each soil was divided into layers with the depth limits 5 to 15 and 25 to 35 cm. from the soil surface. Each soil layer was then dried at room temperature, sifted and thoroughly mixed. This division into layers was made, because McBeth (19) found that the ammonia-fixing power of soil increases with the depth from which it has been taken, with the exception of peat soils which seemed to digress from this rule. The results of these experiments are shown in table 1. The data given are in all cases, here as well as in the following tables, the average of two closely agreeing values. The percentage of nitrogen loss is calculated on the quantity of nitrogen added.

The results obtained accord throughout with those of McBeth, even though the losses here are much smaller. Both of the mineral soils show an increased fixing power by the deeper layer with all concentrations of ammonia, while with the peat soil the result is the reverse of this. It must be pointed out,

TABLE 1

Results of experiments with Boussingault's method

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN			
	Added per 50 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*
Soil I; 5–15 cm..........................	0.00	2.24	....	.....
	10.75	12.60	0.39	3.63
	21.50	22.82	0.92	4.28
	32.26	33.60	0.90	2.79
	53.76	55.16	0.84	1.56
Soil I; 25–35 cm..........................	0.00	2.66	....	.....
	10.75	12.04	1.37	12.74
	21.50	22.26	1.90	8.84
	32.26	33.04	1.88	5.83
	53.76	53.62	2.80	5.21
Soil II; 5–15 cm..........................	0.00	3.50	....	.....
	10.75	12.32	1.93	17.95
	21.50	22.12	2.88	13.40
	32.26	31.92	3.84	11.90
	53.76	52.99	4.27	7.94
Soil II; 25–35 cm..........................	0.00	2.94	....	.....
	10.75	9.66	4.03	37.49
	21.50	18.06	6.38	29.67
	32.26	28.14	7.06	21.88
	53.76	47.95	8.75	16.28
Soil III; 5–15 cm..........................	0.00	7.28	....	.....
	52.64	57.12	2.73	5.19
Soil III; 25–35 cm..........................	0.00	2.66	....	.....
	52.64	53.34	1.96	3.72

however, that the last-mentioned soil was hardly of peat character at the lower depth.

In this connection it is noted that Münter (20) has made comparative investigations between the original form of the Boussingault method, and also of a modified form, by which the distillation was made first after the addition of a neutral salt, e.g., KCl. With zeolites this procedure proved to be effective.

On the contrary, the added ammonia nitrogen could not be recovered from heavy clay soils either with MgO alone or after addition of KCl. The last-mentioned result was confirmed here by investigations on soil II.

<div align="center">THE METHOD OF BARAGIOLA AND SCHUPPLI</div>

The Boussingault method being defective, that of Baragiola and Schuppli (1) was tried. According to the authors this method will solve both phases of the problem.

<div align="center">TABLE 2</div>

<div align="center">*Results of experiments with the method of Baragiola and Schuppli*</div>

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN							
	Baragiola and Schuppli's method				Boussingault's method			
	Added per 50 gm. soil	Found	Lost		Added per 50 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*mgm.*	*per cent*
Soil I; 5–15 cm.	0.00	0.21	.....	.....	0.00	2.24	....	....
	54.15	51.17	3.19	5.89	53.76	55.16	0.84	1.56
Soil II; 5–15 cm.	0.00	0.07	.....	.....	0.00	3.50	....	....
	54.15	46.62	7.60	14.04	53.76	52.99	4.27	7.94
Soil II; 25–35 cm.	0.00	1.89	.....	.....	0.00	2.94	....	....
	54.15	40.81	15.23	28.13	53.76	47.95	8.75	16.28
Soil III; 5–15 cm.	0.00	0.07	.....	.....	0.00	7.28	.....	.....
	54.15	52.29	1.93	3.56	52.64	57.12	2.73	5.19
Soil II; 5–15 cm. (sterilized) ..	0.00	0.91	.....	.....	0.00	3.50	.....	.....
Soil III; 5–15 cm. (sterilized)...	0.00	6.30	.....	.....	0.00	9.38	....	.....

In these experiments it was necessary to use a vacuum of 30 to 40 mm. because of the low water pressure. Because of this, the bath temperature was increased to about 40°C. but even then the distillation required a time of 3 to 4 hours. Further alterations were made in that the receiving flask contained 0.1 N H_2SO_4, and that cochineal was used instead of congo red. The ammonia nitrogen was supplied as previously described in the form of an $(NH_4)_2SO_4$ solution. These results together with those of the Boussingault method are shown in table 2.

The values obtained by the vacuum method for the blank soils are remarkably low. This accords very well with the results obtained by Baragiola and Schuppli, for as a rule they found the soils to be ammonia-free. Only the last two soils, sterilized in an autoclave at 120°C. tor 1½ hours, show ammonia

figures which approach those of the parallel method. This indicates that ammonia was split off from organic nitrogen compounds when the determination was made by the Boussingault method. It is impossible to determine whether the figures obtained for the blank soils by the vacuum method are correct, as this method has been able to liberate the nitrogen added in less degree than the Boussingault method.

THE STEINKOPF METHOD

Some experiments were made also with the Steinkopf (23) vacuum distillation method. This method has not been presented with the present object in view, but it naturally seemed to be adapted for this purpose. The apparatus of Baragiola and Schuppli was used. As before, 5 gm. of MgO and 100 cc. of water were added to 50 gm. of soil. The pressure was about 40 mm. and

TABLE 3

Results of experiments with Steinkopf's method

AMMONIA NITROGEN ADDED PER 50 GM. SOIL	AMMONIA NITROGEN								
	Steinkopf's method			Baragiola and Schuppli's method			Boussingault's method		
	Found	Lost		Found	Lost		Found	Lost	
mgm.	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*per cent*
0.00	0.14	....	.....	1.89	.....	.....	.....	....	....
54.15	42.20	8.09	14.94	40.81	15.23	28.13	.....	....	......
0.00	0.14	....	.....	0.07	.....	.....	2.24	....	....
53.76	50.82	3.08*	5.73	44.59	9.24	17.19	51.66	4.34	8.07

*After the first distillate taken the loss was 6.30 mgm., or 11.72 per cent.

the bath temperature 40°C. The ammonia-free steam was led in through the capillary tube prescribed in the former method. With the first two samples (soil II from 25 to 35 cm.) the distillation was discontinued when the distillate had reached 450 cc.; with the last two (soil II from 0 to 20 cm.), two similar distillates were caught. The results of the experiment are brought together in table 3, where the values obtained by the first vacuum method and the Boussingault method also are shown.

The results show that Steinkopf's method, like the first vacuum method, gives very low ammonia figures for the blank soils. When nitrogen was added, this was liberated most effectively by Steinkopf's method but the yield was not quantitative even when the volume of distillate amounted to 900 cc.

THE POTTER AND SNYDER METHOD

As mentioned before Potter and Snyder among others have shown that the older methods for determination of soil ammonia are incorrect. In this connection they work out a new procedure (21).

As the speed of aeration could not be brought to more than 200 liters per hour in these experiments, the time of treatment was increased to 20 hours. The ammonia nitrogen was supplied as previously described. The results in table 4 show that this method has given about the same result as the two vacuum methods.

<center>MATTHEWS' METHOD</center>

The method by Matthews (18) is based on the same principle as the former method. Matthews, however, uses an apparatus which makes it possible to give an exceedingly thorough treatment to the whole sample during the analysis, whereas in the Potter and Snyder method, at least as it was carried

<center>TABLE 4</center>
<center>*Results of experiments with Potter and Snyder's method*</center>

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN ADDED PER 25 GM. SOIL	AMMONIA NITROGEN				
		Potter and Snyders's method		Boussingault's method		
		Found	Lost		Found	Lost	
	mgm.	mgm.	mgm.	per cent	mgm.	mgm.	per cent
Soil II; 5–15 cm.................. {	0.00	0.07	....	.....	1.82	....	.....
	21.53	17.43*	4.17	19.37	22.40	0.95	4.41
Soil II; 15–25 cm................ {	0.00	0.00	....	.....	3.29	....	.....
	21.53	17.82	3.71	17.23	22.26	2.56	11.89
Soil II; 25–35 cm................ {	0.00	0.00	....	.....	1.37	....	.....
	27.02	20.41	6.61	24.46	22.89	5.50	20.36

*In one of the two parallel trials the receiver was exchanged after 20 hours and the aeration continued for 20 hours more. The loss then decreased to 1.86 mgm., or 8.64 per cent.

out here, it sometimes happens that a part of the sample stays at the bottom of the flask and thus possibly escapes from the effect of the air current.

As a rule, Matthews recovered added ammonia with an accuracy of 98 to 99.5 per cent in 6 hours, and with nearly equal accuracy in 3 hours, when the ammonia nitrogen was added in amounts corresponding to 5.55 and 11.1 mgm. per 100 gm. of soil. With calcareous soils, however, the losses were considerable. Unmanured field soils were found to keep 1.4 to 8.0 mgm. of ammonia nitrogen per kilogram.

In the experiments carried out with this method, Matthews' directions were followed accurately. The time of aeration was in no case shorter than 6 hours. The nitrogen was supplied as previously described. In two cases, noted in table 5, 0.1 N acid and 0.1 N alkali were used instead of the 0.02 N solutions in order to obtain the same degree of accuracy as in the former experiments. Moreover, one experiment was made by which Matthews'

alkaline solution was exchanged by a solution with equivalent amounts of potassium salts.

From table 5 it appears that Matthews' method is not generally applicable. It must be noted that soil II does not belong to that group of soils (calcareous soils) for which the method will give less correct results. This soil was of neutral reaction (pH = 7.1). The experiment with the sand soil (no. IV) has given an unsatisfactory result also. For the blank soils the method has yielded values comparable to those obtained by the vacuum methods and Potter and Snyder's method. In the experiment where Matthews' alkaline solution was exchanged for the corresponding potassium salt solution, the yield is about the same as with the original method.

TABLE 5

Results of experiments with Matthew's method

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN				NOTES
	Added per 25 gm. soil	Found	Lost		
	mgm.	*mgm.*	*mgm.*	*per cent*	
Soil II; 0–20 cm	0.000	0.168	.....	.....	
	2.763	2.688	0.243	8.80	
	12.558	12.089	0.637	5.08	
	0.00	0.00	.....	....	0.1 N acid and alkali
	12.53	11.72	0.81	6.43	0.1 N acid and alkali
Soil II; 25–35 cm	0.00	0.07	.....	....	0.1 N acid and alkali
	12.60	11.17	1.51	11.95	0.1 N acid and alkali
Soil IV; 0–20 cm	0.000	0.168	.....	....	
	12.558	12.264	0.462	3.68	
Soil II; 0–20 cm	0.000	0.168	.....	....	Equivalent K solution
	12.558	11.928	0.798	6.35	Equivalent K solution

THE METHOD OF GIBBS, NEIDIG AND BATCHELOR

Recently Gibbs, Neidig and Batchelor (10) have modified Potter and Snyder's method, in an effort to decrease the time of aeration. They worked with a neutral silt loam soil and succeeded in recovering the nitrogen quantitatively from samples supplied with $(NH_4)_2SO_4$ in an amount corresponding to 43 mgm. of nitrogen per 100 gm. of soil. Their results showed also that nitrogenous organic soil compounds are not split by this method.

The experiments with the addition of $(NH_4)_2SO_4$ have been repeated here following the directions given. After aeration during 1½ hours a new receiving flask was attached and the treatment continued for 1½ hours more.

Table 6 shows that in none of the cases examined has the added nitrogen been recovered quantitatively. That part of it which can be liberated is present in the first distillate. A prolongation of the time of treatment causes a considerable increase of the ammonia figures of the blank samples from which it is evident that organic nitrogen compounds of the soils were attacked.

EXPERIMENTS WITH DIFFERENT EXTRACTING AGENTS

The direct methods having shown their imperfection some further experiments were made on extracting the ammonia nitrogen. Soil II (in the layer from 0 to 20 cm.) was used because it was previously found to be the strongest binder of ammonia. Of the samples supplied with ammonia nitrogen, in each case 50 cc. of $(NH_4)_2SO_4$ solution was added to 100 gm. of soil and this mix-

TABLE 6

Results of experiments with the method of Gibbs, Neidig and Batchelor

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN ADDED PER 100 GM. SOIL	AMMONIA NITROGEN				
		1½ hours' aeration		3 hours' aeration		
		Found	Lost		Found	Lost	
	mgm.	mgm.	mgm.	per cent	mgm.	mgm.	per cent
Soil II; 15–25 cm.	0.00	1.61	.....	.....	3.15	.....	.....
	49.77	47.65	3.73	7.49	49.23	3.69	7.41
Soil II; 25–35 cm.	0.00	0.98	.....	.....	1.47	.....	.....
	49.77	39.76	10.99	22.08	41.02	10.22	20.53
Soil III; 5–15 cm.	0.00	2.03	.....	.....	3.50	.....	.....
	49.77	44.55	7.25	14.57	47.35	5.92	11.89

ture was then shaken repeatedly for 1 hour in a stoppered flask. According to the literature this time is sufficient for the equilibrium between the soil and a solution of an ammonium salt to reach a point very close to the final state of equilibrium. Then 150 cc. of a solution of the various compounds indicated was added in such strength that the concentration after dilution by the liquid already present became that given in the table. The soil water (18.16 per cent), however, was not included here, but was considered in the calculations. When the extracting agents had been added, the mixture was allowed to stand 24 hours as before. The ammonia was then determined by distilling 100 cc. of the filtered extract with an excess of MgO.

The efficiency of the extracting agents of Schlösing and Valmari (0.5 N HCl and 0.5 N NaCl), respectively, as compared with that of water was first determined.

The results in table 7 show that the method of Schlösing, and much less that of Valmari, have not been able to recover the nitrogen added. Compared

with water, the extracting agent of Schlösing has shown the much greater extracting effect as to the nitrogen added, while the salt solution of Valmari

TABLE 7

Results of experiments with the extracting agents of Schlösing and Valmari

EXTRACTING AGENTS	AMMONIA NITROGEN			
	Added per 100 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*
Water............................. {	0.00	0.00	.....	.....
	49.28	14.66	34.62	70.25
0.5 *N* HCl........................ {	0.00	0.84	.....	.....
	50.47	41.54	9.77	19.36
0.5 *N* NaCl....................... {	0.00	0.15	.....	.....
	49.28	27.04	22.39	45.44

TABLE 8

Results of experiments with CaCl₂ as the extracting agent

EXTRACTING AGENTS	AMMONIA NITROGEN			
	Added per 100 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*
0.5 *N* CaCl₂...................... {	0.40*	0.15	0.25	.....
	49.68	32.08	17.60	35.43
1 *N* CaCl₂........................ {	0.80*	0.61	0.19	.....
	50.08	36.96	13.12	26.20
2 *N* CaCl₂........................ {	1.61*	1.68	−0.07	.....
	50.89	40.77	10.12	19.89
4 *N* CaCl₂........................ {	3.22*	2.75	0.47	.....
	52.50	43.52	8.98	17.10
0.5 *N* HCl....................... {	0.00	0.84	.....	.....
	50.47	41.54	9.77	19.36
0.5 *N* HCl plus 0.5 *N* CaCl₂....... {	0.40*	1.15	0.09	.....
	50.87	43.68	8.03	15.79
0.5 *N* HCl plus 1 *N* CaCl₂......... {	0.80*	1.30	0.34	.....
	51.27	43.63	8.48	16.54

* Present in the CaCl₂ solution.

has been rather unimportant. It appears from a later paper by Valmari (26) that he himself has discovered this defect in his method.

A water extract of this present soil contains only a trace of soluble Ca compounds, but after treatment of the soil with $(NH_4)_2SO_4$ solution the test for Ca is unmistakable.   Because of this it was determined to see if an addition of soluble Ca salts would increase the liberation of the ammonia.   The $CaCl_2$

TABLE 9

Results of experiments with potassium and aluminum salts as extracting agents

EXTRACTING AGENTS	pH OF THE EX- TRACTS	AMMONIA NITROGEN			
		Added per 100 gm. soil	Found	Lost	
		mgm.	mgm.	mgm.	per cent
1 N KCl..................................	7.0	0.00	0.00	.....	.....
	7.0	50.12	44.48	5.64	11.26
0.5 N KH₂PO₄............................	5.1	0.00	0.15	.....	.....
	5.1	50.12	35.12	15.15	30.23
1 N KCl plus 0.5 N KH₂ PO₄...............	5.0	0.00	0.15	.....	.....
	5.0	50.12	45.11	5.16	10.30
1 N KCl plus 1.6 gm. KHSO₄...............	4.6	0.00	0.54	.....	.....
	4.6	50.12	45.54	5.12	10.22
1 N Al₂ (SO₄)₃............................	3.6	2.24*	1.22	1.02	.....
	3.6	52.36	38.23	14.13	26.99

*Added with the aluminum salt.

TABLE 10

Results of experiments with methyl and ethyl alcohol as extracting agents

EXTRACTING AGENTS	AMMONIA NITROGEN			
	Added per 100 gm. soil*	Found	Lost	
	mgm.	mgm.	mgm.	per cent
10 per cent methyl alcohol..................	0.00	0.00	.....	.....
	50.26	14.62	35.64	70.91
10 per cent ethyl alcohol...................	0.00	0.46	.....	.....
	50.26	14.70	36.02	71.67
70 per cent ethyl alcohol...................	0.00	0.00	.....	.....
	50.26	0.92	49.34	98.17

preparation used in this experiment was not free from ammonia, as indicated in the following table.   The experiment was completed by an investigation upon the combined effect of $CaCl_2$ and HCl.   The results of the experiment appear in table 8.   The former results from the extraction with 0.5 N HCl

·have been included. The losses obtained after treatment with 0.5 N HCl plus CaCl$_2$ solution have been calculated on the soil ammonia figure of the Schlösing method as standard.

It was thought that the results from some experiments by Cook (9) and McBeth (19) might indicate more effective extracting agents. Cook determined the ammonia adsorption by treating 50 gm! of soil with 200 cc. of 0.01 N (NH$_4$)$_2$SO$_4$, after which the amount of ammonia unfixed was obtained by distilling an aliquot of the filtered extract with NaOH. When he added small amounts of K$_2$SO$_4$, KCl or acid phosphate to the soil before the addition of the (NH$_4$)$_2$SO$_4$ solution, as a rule he found a distinct decrease of the adsorption of ammonia. McBeth, extracting his soils with HCl according to Schlösing, found for one soil by supplying 10 cc. of 1 N Al$_2$(SO$_4$)$_3$, AlCl$_3$, or Al(NO$_3$)$_3$ to 100 gm. of soil 30 minutes before the addition of (NH$_4$)$_2$SO$_4$ (50 mgm. of N), that the amount of ammonia retained was reduced from 47 to about 11 per cent. When he exchanged the Al salts with the equivalent amounts of K salts for the same soil this amount of ammonia was brought down to about 6 per cent.

With these results in mind the following experiments, the data of which are given in table 9, were made. The combination of 1 N KCl with 1.6 gm. of KHSO$_4$ was undertaken since a preliminary experiment had shown that this amount of KHSO$_4$ gave a lower pH value to the extract than did .1 N KCl plus 0.5 N KH$_2$PO$_4$. The pH values were determined colorimetrically on the filtered soil extracts. The aluminum sulfate employed was not free from ammonia.

Compared with pure water (table 7) all these extracting agents have liberated considerably more of the nitrogen added. This is especially true where KCl was used either alone or together with KH$_2$PO$_4$ or KHSO$_4$. Naturally this is allied to the special position of the K and NH$_4$ ions in adsorption in the soil, which is opposite to that of the other cations. Al$_2$(SO$_4$)$_3$ was found to be much less effective than in McBeth's experiments. The results shown in table 9 indicate that an increase of the hydrogen-ion concentration of the extract cannot play any important part in the liberation of ammonia from this neutral soil. This fact will be still more obvious if the pH value obtained in the extraction according to Schlösing also is considered. This pH determination, performed by Biilmann's quinhydrone method (8), gave the result pH = 0.5. At the same time (table 7) a considerably smaller amount of ammonia was recovered than by extraction with KCl.

All the former extracting agents except the hydrochloric acid have a greater surface tension than the water, and, as the hydrochloric acid sets free a strong concentration of salts from the soil, the result in this case also is an extracting agent of the same kind. As it was thought of interest to find out how solutions of a smaller surface tension than that of water acted, the experiments reported in table 10 were made.

Both the 10 per cent solutions have given the same result as pure water (table 7). The concentrated ethyl alcohol has removed only 0.92 mgm. of the nitrogen added, corresponding to 4.34 mgm. of $(NH_4)_2SO_4$, while the volume of liquid used should have been able to dissolve about 680 mgm. of this salt.

EXPERIMENTS WITH REPEATED SUCCESSIVE EXTRACTIONS

Experiments to leach added ammonia with water have shown that a quantitative recovering in this way is not to be expected. Cook (9) tried two methods of procedure for determination of the adsorbing power of the soil. That method which was used in his later investigations has been previously described. The second method was as follows: 50 gm. of soil were placed on a filter and then 8 cc. of 1 N $(NH_4)_2SO_4$ was added. The soil was brought to optimum moisture and allowed to stand for 4 hours, after which it was leached with water. The successive 200-cc. portions of the filtrate were then analyzed for ammonia. Cook found that practically all the ammonia nitrogen which could be extracted in this way was present in the first portion. McBeth (19), who added 50 mgm. of ammonia nitrogen per 100 gm. of soil found for one of the soils examined by leaching with water, that 23 per cent of this nitrogen was present in the first 400-cc. portion and after collecting six similar portions the yield had risen to 33 per cent. When the same soil was leached with hydrochloric acid, the corresponding figures were 52 and 81 per cent. The above results did not encourage the use of water or hydrochloric acid in leaching experiments. However, it might be expected that a potassium salt solution would be more suitable for this purpose, partly because of McBeth's results after addition of K salts and partly because of the experiments previously described in which the KCl solution was found to be the most effective agent. Some experiments by Kellner may be interpreted in favour of this assumption. Having found that the soil adsorbs the K and NH_4 ions in equivalent amounts (12), he worked out a method (13), for the determination of assimilable potassium of the soil, by which the potassium was extracted successively with a hot NH_4Cl solution. If this procedure is of general application it might be possible to liberate all the soil ammonia by inverting the method, that is by exchanging NH_4Cl for KCl. For this, however, one needs to work at room temperature or lower. McBeth (19) found for one soil that the amount of ammonia fixed rose from 45 to 65 per cent when the temperature of the soil was increased from 5 to 100°C. For another soil these percentages were 75 and 87 respectively. That high temperatures are not necessary is a fortunate circumstance, for with an increase in temperature there is a greater risk of splitting off ammonia from the organic nitrogen compounds of the soil.

For the next experiment Kellner's method consequently was altered to the following procedure: 25 gm. of soil was placed in a beaker and 12.5 cc. of $(NH_4)_2SO_4$ solution added. The mixture was repeatedly stirred for 1 hour.

Then 50 cc. of 3.5 N KCl solution was added, the contents of the beaker were stirred from time to time and then allowed to settle, and after $\frac{1}{2}$ hour in all the solution was decanted to a filter which held exactly 50 cc. Again 50 cc. of the KCl solution was added to the residue in the beaker and the treatment was repeated until 20 filtrates had been secured. Two ammonia determinations were made on each sample; the first ten filtrates being combined for one determination and the following ten filtrates combined for the other determination. The determinations were made by distilling with MgO, the ammonia liberated being caught in 0.02 N H_2SO_4, which afterwards was titrated with 0.02 N NaOH, methyl red being used as the indicator. Each filtrate was tested for ammonia with Nessler's reagent. As the successive filtrates from the blank sample also showed a strong ammonia reaction, the KCl solution (prepared with Kahlbaum's KCl "Zur Analyse") was examined with the same

TABLE 11

Results of a preliminary experiment in inversion of Kellner's method

AMMONIA NITROGEN ADDED PER 100 GM. SOIL*	AMMONIA NITROGEN			
	Extracts 1–10		Extracts 11–20	
	Found	Lost	Found	Lost
mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
0.000	1.414	0.335	1.554	0.195
12.530	13.090	1.189	1.540	0.209

* The nitrogen of the KCl solution not included.

reagent and it was then found to contain ammonia. A quantitative determination found 1.749 mgm. of ammonia nitrogen per 500 cc. of the KCl solution. The experiment is recorded in table 11.

It is evident that this experiment does not indicate the adaptability of the procedure for the purpose in question. In fact, the soil had been treated uninterruptedly with a dilute solution of ammonia. Since the definite equilibrium between the soil and this solution has been maintained, the latter will leave the soil with an unaltered concentration of NH_4. This also may be seen from the experiment.

In order to obtain a better idea of the last method the work was continued with ammonia-free KCl solution, prepared by boiling a concentrated solution of KCl and KOH until the ammonia was driven off, after which the solution was neutralized with ammonia-free HCl. As the 3.5 N KCl leaves a troublesome salt crust on the filter, some comparative experiments were made with 3.5 and 0.5 N KCl, and it was found that the weak solution was quite as available as the stronger one by this procedure. Because of this the extractions in the later experiments were carried out with 0.5 N KCl. It was also evident that the use of 0.02 N H_2SO_4 and 0.02 N NaOH meant a superfluous refinement of the method, so these solutions were exchanged for the 0.1 N

solutions. In order to decrease the experimental error all the filtrates were collected in the same Florence flask, which, after addition of MgO, was attached to the distilling apparatus. Only in those cases where twenty or still more filtrates were caught the ammonia determination was made on an aliquot of the combined filtrates. The samples with $(NH_4)_2SO_4$ added were extracted in this way until the filtrate no longer gave a coloration with Nessler's

TABLE 12

Results of experiments on different mineral soils with successive extractions with 0.5 N KCl

NUMBER AND DEPTH OF THE SOIL SAMPLE	SOIL	NUMBER OF EXTRAC- TIONS	AMMONIA NITROGEN			
			Added per 25 gm. soil	Found	Lost	
			mgm.	mgm.	mgm.	per cent
Soil I; 0–20 cm..................	Silt loam	12	0.00	0.14	......	......
		12	12.64	12.46	0.32	2.53
Soil II; 5–15 cm..................	Heavy clay	15	0.00	0.00	......	......
		15	12.04	12.15	−0.11	−0.87
Soil II; 0–20 cm	Heavy clay	15	0.0	0.07	......	......
		15	12.64	12.35	0.36	2.81
Soil II; 15–25 cm.................	Heavy clay	15	0.00	0.25	......	......
		15	12.60	12.32	0.53	4.21
Soil II; 25–35 cm.................	Heavy clay	15	0.00	0.14	......	......
		15	12.04	10.33	1.85	15.44
Soil IV; 0–20 cm..................	Sand	10	0.00	0.04	......	......
		10	12.57	12.56	0.05	0.36
Soil V; 0–20 cm..................	Sand	10	0.00	0.42	......	......
		10	12.60	12.92	0.10	0.83
Soil VI; 0–20 cm..................	Loam	10	0.00	0.00	......	......
		10	12.64	12.74	−0.10	−0.79

reagent, and for the sake of uniformity the same number of extractions were performed on the blank samples.

In table 12 a number of experiments on mineral soils, carried out by this new procedure, are brought together.

It appears from table 12 that the procedure here used must be considered quite satisfactory in the case of surface soils, or those taken from the depth of 0 to 20 cm. However, it did not succeed in recovering all the added ammonia from the lower layers of the heavy clay soil. Other experiments made with this soil are reported later.

No long period of time should elapse between the successive extractions. If, for example, the soil suspension is set aside until the following day a distinct ammonification sets in. This, however, can be prevented by the addition of 1 to 5 gm. of $HgCl_2$ to each liter of 0.5 N KCl. Special experiments showed that such an addition of $HgCl_2$ will not influence the extracting power of the solution. In these instances the ammonia distillations were of course made after the mercury was precipitated as HgS. The use of this last extracting agent has the disadvantage that the extracting process cannot be followed with Nessler's reagent, because of the brown precipitate which is formed by Nessler's solution in the presence of $HgCl_2$.

TABLE 13

Results of experiments on peat loam soils with successive extractions with 0.5 N KCl

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN			
	Added per 25 gm. soil	Found	Lost	
	mgm.	mgm.	mgm.	per cent
Soil III; 5–15 cm............................ {	0.00	0.00	......	......
	12.04	12.01	0.03	0.29
Soil VII; 0–20 cm............................ {	0.00	0.07	......	......
	12.57	12.67	−0.03	−0.24

TABLE 14

Results of experiments to determine the effect of lime upon extraction

ADDITIONS PER 25 GM. SOIL		AMMONIA NITROGEN			NOTE
CaCO₃	NH₄-N	Found	Lost		
gm.	mgm.	mgm.	mgm.	per cent	
0.0	0.00	0.04	....	....	
2.0	12.57	12.36	0.25	2.03	
2.0	12.57	12.53	0.08	0.64	The first extraction with HCl

In the case of peat soils where there is much material which will not settle, the following procedure was used: 25 gm. of soil was placed on a hardened filtered in a Büchner funnel fixed to a suction flask, and 12.5 cc. of a solution of $(NH_4)_2SO_4$ added. After 1 hour 50 cc. of 0.5 N KCl was added, the mixture stirred for a few minutes with a ball-tipped glass rod and then extracted by suction. After the suction had been stopped, 50 cc. more of the KCl solution was added and the treatment was repeated until 10 extractions had been made. Then the ammonia determination was made as usual on the combined filtrates. The results from two similar experiments with peat loam soils are brought together in table 13. The filtered extracts of both these soils being quite yellow, no examination with Nessler's reagent was made.

Table 13 shows the sufficiency of 10 extractions for the quantitative recovery of the ammonia added from both of the peat soils. The method being satisfactory, no experiments were made to find out if the same results might be had with fewer extractions.

For all the blank samples the new method has given very low ammonia figures. It is to be noticed, however, that hardly one of the examinations was made directly on fresh soil but at first on soil which for a shorter or longer time had been stored in the laboratory. As some of the soils had been dried to such an extent that they could be easily sifted, all the conditions for a rapid nitrification were present, and of course the ammonia nitrogen was used up in this process. Since the ammonia added was recovered from the soils

TABLE 15

Results of single-extracting experiments with 0.5N KCl

NUMBER AND DEPTH OF THE SOIL SAMPLE	SOIL	AMMONIA NITROGEN			
		Added per 100 gm. soil	Found	Lost	.
		mgm.	*mgm.*	*mgm.*	*per cent*
Soil I; 0–20 cm..............	Silt loam {	0.00	0.00	....	.....
		50.26	46.60	3.66	7.28
Soil II; 0–20 cm..............	Heavy clay {	0.00	0.00	....	.....
		50.26	44.29	5.97	11.89
Soil V; 0–20 cm.	Sand {	0.00	0.00	....	.....
		50.26	50.05	0.21	0.43
Soil VI; 0–20 cm..............	Loam {	0.00	0.00	....	.....
		50.26	48.09	2.17	4.32

examined, with the exceptions noted, the low ammonia figures of the blank soils are good proof that the organic nitrogen soil compounds are not attacked by this method.

Lemmermann and Fresenius (17), as well as Ruprecht and Morse (22), have found that lime (in the form of $CaCO_3$) is one of the factors contributing to the ammonia-adsorbing power of soil. As all the soils here examined were neutral or acid this point remained to be examined. For that reason the following experiment, reported in table 14, was made with soil V. Two samples, of 25 gm. each, were mixed with 2 gm. of finely ground $CaCO_3$, after which a solution of $(NH_4)_2SO_4$ was added. After 1 hour one sample was extracted successively with 0.5 N KCl. To the other sample 50 cc. of ammonia-free HCl was added in an amount equivalent to the lime previously used. Since the solution had been decanted to the filter, the extractions were continued successively with 0.5 N KCl. In both cases the tenth extract was free from ammonia.

Though the lime was supplied in an amount much greater than is ever used in practice, its effect was quite unimportant. However, as better results were obtained in the case where the lime was transformed into chloride, it will be good to neutralize the alkaline soils with hydrochloric acid before starting the extractions.

It was discovered only after these and later experiments had been made that Tarassoff (24) had already determined soil ammonia by extracting it with a KCl solution. His method was as follows: 500 gm. of soil was shaken in a 1-liter cylinder with 800 cc. of 5 per cent solution of KCl. Thereupon the whole content of the cylinder was brought cautiously to a filter and the soil carefully washed with the solution of KCl. The consecutive portions of the filtrate were analyzed separately by distilling with MgO. With black soils rich in humus this method gave *more*, and with clay soils *less*, ammonia nitrogen than did Schlösing's method. Tarassoff, however, made no control experiments with the addition of ammonia nitrogen and it seems to be very unlikely that the method used in such a case would have been satisfactory,

TABLE 16

Results of experiments with the extracting ratio 1:4

AMMONIA NITROGEN			
Added per 25 gm. soil	Found	Lost	
mgm.	*mgm.*	*mgm.*	*per cent*
0.00	0.07	....	....
2.48	2.52	0.03	1.21
12.39	12.32	0.14	1.13

at least with a reasonable quantity of solution. König (16) seems to be of the opinion that in the treating of soil with a KCl solution all the ammonium compounds are brought into solution in one extraction by means of an inter-change of ions. That this view cannot be correct and that, on the contrary, a definite equilibrium will exist between the soil and the extracting agents, appears from the result, reported in table 9, of a single extracting experiment on soil II with 1 N KCl. In order to illustrate this question the single extracting experiments with 0.5 N KCl (table 15) were made. In this the extracting ratio 1:2, i.e. 1 part of soil and 2 parts of solution, and the same procedure, were used as in the earlier single extracting experiments.

Thus it has happened that only with the sandy soil was all the ammonia liberated quantitatively; while with the other soils a part of the added ammonia is fixed in some manner.

For peat soils there is no reason to change the present successive procedure with the extracting ratio 1:2, but for mineral soils this manner takes considerable time, as sometimes up to 15 extractions are required before all the ammonia is liberated. By increasing the extracting ratio, for example to 1:4, a quicker extraction is to be expected partly because a little more of the am-

monia is extracted in each extraction, as experiments with single extractions have shown, and partly because the absolute amount of ammonia already liberated, which remains in the beaker after each decantation to the filter, is reduced. Since soil II retained the ammonia more obstinately than any other surface soil (table 12), the following experiment was made with it, the data of which are given in table 16. Twenty-five gm. of the soil was placed in a 250-cc. beaker and 12.5 cc. of a solution of $(NH_4)_2SO_4$ or 12.5 cc. of water added. After 1 hour the successive extractions were made in the same manner as before, but with 100-cc. portions of 0.5 N KCl. After 7 extractions, which required 5 hours, the liberation of ammonia was completed. Thus by enlargement of the extracting ratio from 1:2 to 1:4, the number of extractions could be reduced one-half.

FURTHER EXPERIMENTS WITH THE HEAVY CLAY SOIL (NO. II)

As pointed out before, the ammonia added could not be recovered from the lower layers of the heavy clay soil (table 12). For the layer 15 to 25 cm. the loss was relatively small but for the lowest layer (25 to 35 cm.) it was very considerable. Experiments both with 20 and 30 successive extractions (in the extracting ratio 1:2) could not alter this result. The three samples from the layers 5 to 15, 15 to 25 and 25 to 35 cm., hereafter referred to as A, B, and C, respectively, had been cut out from one and the same block of soil, taken from a part of the field which had not been tilled during the last 9 months. These samples showed the pH values 6.2, 6.2 and 7.0 respectively. A chemical analysis gave the values indicated in table 17.

The organic matter was determined as loss after ignition minus H_2O. The K_2O, P_2O_5, CaO, and Al_2O_3 plus Fe_2O_3 were determined after digestion for 1 hour with 20 per cent HCl. Assimilable lime was obtained after treatment with a 10 per cent solution of NH_4Cl.

The most remarkable differences between the three samples from the chemical point of view are that the percentage of organic matter decreases with the depth of soil, whereas the percentage of Al_2O_3 plus Fe_2O_3 varies somewhat in the reverse order.

The experiments with soil C presented in table 18 were made by means of the successive extracting procedure in the extracting ratio 1:2. In all cases 12.5 cc. of $(NH_4)_2SO_4$ solution or an equal volume of water was added to 25 gm. of soil and then stirred from time to time for 1 hour. In one experiment (no. 1 and 2) the first extraction was made with 50 cc. of ammonia-free 0.5 N HCl. This was intended partly to reduce the pH value of the soil, as this soil had a higher pH value than the extractable soil A, and partly to diminish the percentage of Al_2O_3 plus Fe_2O_3. In the next experiment (no. 3 and 4) 5 gm. of soil III, earlier found to be free from ammonia, was added immediately before extracting in order to increase the percentage of organic matter. In the third experiment (no. 5 and 6), 5 gm. of soil III and 10 gm. of sand were added at the same time. In agricultural practice sand and mould are

added to clay soils in order to diminish the great cohesion in the clay and to counteract its tendency to pack or puddle. In the fourth experiment (no. 7 and 8) the extractions were made at a temperature of 3 to 5°C. on account of McBeth's results (19) from investigations concerning the influence of temperature on ammonia adsorption. Having stood for 1 hour at room temperature with 12.5 cc. of $(NH_4)_2SO_4$ or 12.5 cc. of water, these samples were placed

TABLE 17

Chemical analyses of heavy clay soil II

SOIL	PER CENT OF AIR-DRIED SAMPLE		PER CENT OF DRY MATTER						
	Particles > 2 mm.	H₂O	Organic matter	Total nitrogen	K₂O	P₂O₅	CaO	Al₂O₃ + Fe₂O₃	Assimilable CaO
A	0.70	12.90	8.01	0.29	0.74	0.31	1.06	9.65	0.50
B	0.35	13.21	7.52	0.28	0.78	0.27	1.08	9.90	0.50
C	0.23	12.17	5.00	0.17	0.70	0.21	1.12	11.20	0.55

TABLE 18

Results of extracting experiments with heavy clay soil II from depth of 25 to 35 cm.

NUMBER	AMMONIA NITROGEN				NOTES
	Added per 25 gm. soil	Found	Lost		
	mgm.	*mgm.*	*mgm.*	*per cent*	
1	0.00	0.28	....	.....	}Extraction 1 made with 0.5 *N* HCl
2	12.57	10.43	2.42	19.26	
3	0.00	0.11	....	.....	}Addition of 5 gm. of peat soil
4	12.41	9.73	2.79	22.48	
5	0.00	0.11	....	.....	}Addition of 5 gm. of peat soil plus 10 gm. of sand
6	12.41	9.73	2.79	22.48	
7	0.00	0.21	....	.....	}Extractions made at 3–5°C.
8	12.60	10.36	2.45	19.45	
9	0.00	0.11	....	.....	}Extractions made with 3*N* KCl
10	12.41	10.08	2.44	19.67	

in ice water and then the extractions were made with KCl solution, previously cooled down to about 3°C. An experiment (no. 9 and 10), also was conducted in which the extractions were made with 3 *N* KCl in order to show that an increase of the concentration of the extracting agent is without any effect. In all these experiments the fifteenth filtrate was free from ammonia.

Thus this soil retains a rather constant amount of the ammonia added irrespective of the method of treatment. Nor could this part be liberated

by increasing the temperature as found by a further experiment on the samples 7 and 8. When the related 15 extractions had been made these samples were placed at the steam bath and stirred with 50 cc. of KCl solution, previously heated to 80°C. The samples then were allowed to settle on the bath, whereupon the extracts were decanted to the filter, 5 similar extractions being made. In no case was ammonia liberated by this procedure.

Finally, mechanical analyses of the soils A, B and C were made, giving the percentages shown in table 19. At first the gravel was sifted off and therefore the results refer to particles less than 2 mm. in diameter.

The table shows that the most remarkable difference between the samples exists in the percentage of clay, soil C holding about 13 per cent more of clay than the others. Naturally this higher percentage of clay in itself cannot be sufficient to account for the ammonia retention. The mechanical analysis gives no information, beyond the upper limit, of the size of the clay particles, but because of sedimentation the percentage of the smallest clay

TABLE 19

Mechanical analyses of heavy clay soil II

SOIL	SIZE OF PARTICLES						
	2–0. 6 mm.	0. 6–0.2 mm.	0, 2–0.06 mm.	0, 06–0.02 mm.	0, 02–0.006 mm.	0.006–0, 002 mm.	<0.002 mm. (clay)
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A	1.79	6.17	13.17	11.18	10.05	11.72	45.92
B	1.85	7.00	13.12	10.60	10.00	12.35	45.08
C	2.01	5.21	10.07	9.93	9.30	12.14	51.34

particles may increase with the depth of the soil layer. The fixation of a part of the added ammonia by soil C therefore may probably be attributed to the surface effect of the very finest clay particles.

On the basis of the results the following method for determination of ammonia in surface soils is presented:

Mineral soils. In a 200 to 250 cc. beaker, 25 gm. of soil is stirred for a few minutes with 100 cc. of 0.5 N KCl solution free from ammonia. After settling, the solution is decanted to a filter of 100 cc. capacity. Then 100 cc. of the KCl solution is added to the beaker again and the treatment is repeated until the filtrate gives no coloration with Nessler's reagent. Even for soils which in consequence of colored filtrates do not permit examination with this reagent, not more than seven successive extractions are required. Alkaline· soils should first be neutralized with ammonia-free hydrochloric acid. Then the combined filtrates are distilled with MgO, the ammonia being caught in 0.1 N H_2SO_4. When distillation is finished the carbon dioxide is removed from the distillate by boiling, and after cooling the distillate is titrated with 0.1 N NaOH, methyl red being used as the indicator. A blank determination should be made on the reagents.

Peat soils. Twenty-five grams of soil is placed on a hardened filter in a Büchner funnel fixed to a suction flask, and 50 cc. of 0.5 N KCl solution is added. The soil is then stirred by means of a ball-tipped glass rod, after which the solution is sucked off. Then the suction is stopped and 50 cc. of the KCl solution is added again to the soil, whereupon the treatment is repeated until all the ammonia is extracted. Not more than 10 extractions are required at the most. The ammonia determination is performed in the same manner as for the mineral soils.

By extracting with 0.5 N KCl solution containing 1 to 5 gm. of $HgCl_2$ per litre, the work can be interrupted without any risk of ammonification and finished another day. In this case the mercury must be precipitated as HgS before the distillation. A disadvantage following the use of KCl solution containing $HgCl_2$ is that this solution, even if free from ammonia, gives a brown precipitation with Nessler's reagent.

Of course there is no objection to working with a larger quantity of soil, in order to obtain better mean values. In such a case the KCl portions must be increased in corresponding degree.

SUMMARY

1. A reëxamination of the methods of Boussingault, Baragiola and Schuppli, Potter and Snyder, Matthews and that of Gibbs, Neidig and Batchelor for the determination of ammonia in soil showed that none of them was able to recover added ammonia quantitatively. This was true for both surface soils and subsoils.

2. Steinkopf's steam distillation was not suitable for the purpose in question.

3. Experiments with different extracting agents showed that as a rule it is not possible to bring all the added ammonia into solution in one extraction. Therefore, the methods of Schlösing and Valmari cannot be of general application.

4. As to the liberation of added ammonia, a solution of potassium chloride was found to be the most effective of the extracting agents examined.

5. Added ammonia was recovered quantitatively from *surface soils* by means of a successive extracting procedure.

By this method, in case of a mineral soil, 25 gm. of soil is extracted successively with, at the most, seven 100-cc. portions of approximately 4 per cent potassium chloride solution. With peat soils, 25 gm. of soil is extracted in a similar way with at most ten 50-cc. portions of the same solution.

The very low ammonia values found by this method for untilled arable soils are strong evidence that organic nitrogen compounds of soil are not split during the analysis.

6. The successive extracting procedure was not satisfactory in case of a heavy clay subsoil taken from the depth of 25 to 35 cm. This may be attributed to the surface effect of the very finest clay particles.

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THE INFLUENCE OF PHOSPHATE, BIPHOSPHATE, CARBONATE, SILICATE AND SULFATE OF CALCIUM, SODIUM AND POTASSIUM ON PLANT GROWTH IN ACID MINERAL SOILS

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INTRODUCTION

The study of the nature and the improvement of acid mineral soil is very important to the agriculture in our country where acid mineral soil is widely distributed. (13, 27, 49).

Though there are many opinions about the cause of the acidity of soil, (15, 18, 19, 20, 21, 25, 26, 30, 39, 41, 42, 53, 55, 58, 59) it seems to be recognized that aluminium is present in greater amount in acid soil than in non-acid soil and is concerned directly or indirectly with its acidity (1, 13, 22, 32, 34, 35, 37, 38, 42, 43, 44, 46, 52). The toxic action of aluminium upon plant growth has been well proved by various authors (9, 11, 17, 24, 28, 31, 33, 56, 60). Abbott, Conner and Smalley (1) studying the cause of unproductive acid soil of Indiana, found that a relatively large amount of aluminium was dissolved out in the soil extract and that the toxicity of the extract was equal to the toxicity of nitric acid and aluminium nitrate of the same normality. Ruprecht and Morse (44) found that aluminium sulfate formed by the continual application of ammonium sulfate is the cause of unproductivity of soil. Hartwell and Pember (23) also found that aluminium is the element responsible for the depression of the growth of barley. Mirasol (32) also confirmed, this effect on the growth of sweet clover. Blair and Prince (4) recently found that aluminium present in great amount in the soil solution extracted by distilled water, is the cause of toxicity of soil.

Aluminium can not be neglected as one of greatest factors causing unproductivity of acid soil, though there may be some other injurious factors such as lack of plant nutrients. The elimination of active aluminium through changing it into an insoluble form by the addition of lime or other salts, therefore, should bring some favorable effect upon the plant growth. Studying the effect of silicates upon the growth of plants in acid soil, Cowles (12) and Scheidt (45) reported that dicalcium silicate had a relatively greater value than either ground limestone or calcium hydrate as a fertilizer material. Hartwell and Pember (23), and Schollenberger (47) also reported that plants made a favorable growth by the application of dicalcium silicate to acid soil. Conner (8)

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reported that dicalcium silicate gave better results in field and pot experiments than those obtained by the use of lime.   The superior effect of silicate was attributed to the elimination of aluminium as aluminium silicate from the soil solution.   The effect of the addition of calcium carbonate to acid soil also is well known.   As to the cause of its favorable effect, Ruprecht and Morse (44) suggested that aluminium in soil is precipitated as hydroxide upon the addition of calcium carbonate, and as such has no effect on plant growth.   Mirasol (32) reported also that the good effect of carbonate for the correction of unproductive acid soil is due to the elimination of active aluminium because when calcium carbonate is added to acid soil aluminium is transformed into some very stable compound such as calcium aluminate.   The favorable effect of phosphate upon the growth of plants in the acid soil also is a well known fact, since the addition of phosphates is believed to cause the formation of the very insoluble aluminium phosphate, otherwise it acts upon the plant growth harmfully. After the investigation of the effect of the addition of biphosphate, Hartwell and Pember (22) found that the amount of active aluminium was decreased and barley made remarkable growth.   Mirasol (32) studied the same subject and reported that sweet clover also made marked growth by the addition of biphosphate to the acid soil.

Thus, the elimination of soluble aluminium existing in acid soil is a very important phase of the problem of improving unproductive acid soil.   Thus the addition of some chemicals which make aluminium insoluble is expected to be favorable to plant growth.   The investigations hitherto conducted, however, are not, satisfactory regarding this phase of the problem.   The investigators have not paid any attention to the power of the chemicals used to make aluminium insoluble.   Then, we have undertaken the experiment for the purpose of throwing more light upon the general problem of aluminium in acid soils, and also to explain why   phosphate fertilizer has a good effect on such soil.

EXPERIMENT I

The depression of the toxic action of aluminium compounds would be expected to correspond with the power of the various chemicals which convert the soluble into the insoluble compounds, and the favorable action of the various chemicals upon the plant growth should be due to this power. Also, it is important to know how much soluble aluminium is converted into insoluble by the addition of the chemicals andt heir relation to the plant growth. In order to throw some light upon these questions, an experiment was conducted on the use of the phosphate, biphosphate, carbonate and silicate of sodium.

At first the amount of insoluble aluminium produced by mixing a solution of equal volume of $0.2N$ or $0.1N$ aluminium chloride and $0.2\ N$ or $0.1\ N$ sodium silicate, sodium carbonate, sodium phosphate and sodium biphosphate was determined as a measure of the power of these chemicals to convert the soluble into the insoluble compound.   The results are given in table 1.

The composition of the aluminium silicate produced from the mixture of aluminium chloride and sodium silicate was not definite. While a large amount of silica was precipitated, the amount of precipitated aluminium was very small. This may be due to either the fact that the form of aluminium silicate is very complex, or that silica is liberated from sodium silicate by the action of hydrochloric acid formed by the hydration of aluminium chloride and precipitated with aluminium silicate. No insoluble aluminium was obtained from the mixed solution of sodium biphosphate and aluminium chloride. It was observed that 30 per cent of the original aluminium and phosphoric acid was precipitated from the mixed solution of sodium phosphate and aluminium chloride. This small amount of the precipitate produced may be due to the acid reaction of the mixture. The amount of aluminium pre-

TABLE 1

Amount of aluminium precipitated from mixed solution of 100 cc. of aluminium chloride and 100 cc. of sodium silicate, sodium carbonate, sodium phosphate or sodium biphosphate

CONSTITUENTS MEASURED	NAME OF MIXED SALTS			
	Sodium silicate + aluminium chloride	Sodium carbonate + aluminium chloride	Sodium phosphate + aluminium chloride	Sodium biphosphate + aluminium chloride
A—0.2 N Salts				
	gm.	gm.	gm.	gm.
P_2O_5	—	—	0.1447	—
SiO_2	0.1810	—	—	—
Al_2O_3	0.0220	0.3400	0.0973	—
B—0.1 N Salts				
	gm.	gm.	gm.	gm.
P_2O_5	—	—	0.0871	—
SiO_2	0.1184	—	—	—
Al_2O_3	0.0232	0.1634	0.0566	—

cipitated in this case, however, was larger than that precipitated from the mixed solution of aluminium chloride and sodium silicate. In the case of mixing aluminium chloride and sodium carbonate, the entire amount of aluminium was precipitated, the reaction of the mixture being alkaline.

In order to confirm these phenomena as occurring in the soil, in the next experiment these solutions were added to the acid soil, and then a soil solution was prepared with water five times the weight of the soil. The amounts of alumina, silica and phosphoric acid in the solution were measured, with following results in table 2.

When sodium carbonate solution was added to the soil which had been treated with aluminium chloride solution, aluminium was scarcely found in the soil solution. The alkalinity of sodium carbonate was higher than of phosphate and silicate of sodium, and therefore a large amount of aluminium was

precipitated and retained in the soil as compared with the latter two salts. When 0.2N sodium phosphate was used, one-thirteenth of the original aluminium which had been added to the soil was dissolved out while no phosphoric acid was found in the solution extracted from the soil. When 0.1 N sodium phosphate was used, neither aluminium nor phosphoric acid was detected. When 0.2N or 0.1N sodium biphosphate was added, one-third of the original amount of aluminium which had been added to the soil was found again in the solution, a trace of phosphoric acid. Though biphosphate could not produce

TABLE 2

Amount of aluminium in the solution extracted from 200 gm. of soil with five times its weight of water

(1)   100 cc. aluminium chloride and 100 cc. sodium silicate, sodium carbonate, sodium phosphate or sodium biphosphate added.

CONSTITUENTS MEASURED	NAME OF MIXED SALTS			
	Sodium Silicate + aluminium chloride	Sodium carbonate + aluminium chloride	Sodium phosphate + aluminium chloride	Sodium biphosphate + aluminium chloride
A—0.2 N Salts				
	gm.	*gm.*	*gm.*	*gm.*
P_2O_5...............	—	—	—	Trace
SiO_2...............	0.0340	Undetermined	Undetermined	Undetermined
Al_2O_3...............	0.1540	—	0.0200	0.1046
B—0.1 N Salts				
	gm.	*gm.*	*gm.*	*gm.*
P_2O_5...............	—	—	—	Trace
SiO_2...............	0.0230	Undetermined	Undetermined	Undetermined
Al_2O_3...............	0.0440	—	—	0.0534

(2)   100 cc. of aluminium chloride solution only added

NORMALITY	CONSTITUENTS MEASURED	AMOUNT OF ALUMINA PRESENT IN ORIGINAL SOLUTION	AMOUNT OF ALUMINA PRESENT IN EXTRACTED SOLUTION
		gm.	*gm.*
0.2 N	Al_2O_3	0.3680	0.2640
0.1 N	Al_2O_3	0.1840	0.0880

any precipitate of aluminium phosphate from aluminium chloride and sodium biphosphate in the solution, a relatively great amount of aluminium was precipitated in the case of the soil. It was known further from the results that almost the total amount of phosphoric acid was retained in the soil without relation to the amount of aluminium retained, when sodium phosphate or sodium biphosphate was added with aluminium chloride. When 0.2 N sodium silicate was used, one-ninth and two-thirds, respectively, of the original amount of silica and aluminium which had been added to the soil were found in the soil solution. And when 0.1N solution also was used, one-seventh and one-half

of the original amount of silica and aluminium, respectively, were detected in the soil solution. It was observed, therefore, in this case, that a large amount of aluminium which had been added was dissolved out again in the soil solution without being retained with silica in the soil. Although, the reaction of sodium silicate in the solution is more alkaline than that of sodium phosphate and biphosphate, the former could not precipitate the aluminium as much as the latter two salts, except when 0.1 N of sodium biphosphate was used.

When aluminium chloride solution only was added to the soil, one-fourth to one-half of original amount of aluminium was retained by the soil; but this was smaller than that held after the addition of sodium carbonate, sodium phosphate, sodium biphosphate or sodium silicate. From this it is clear that some soluble aluminium in the soil is transformed into insoluble and retained in it by the addition of carbonate, phosphate, biphosphate and silicate of sodium. The order of the salts in precipitating aluminium in the solution is— carbonate, phosphate and silicate, while the order in bringing aluminium into insoluble form in the soil is—carbonate, phosphate, biphosphate and silicate.

EXPERIMENT II

It is reported that the addition of the carbonate, phosphate, biphosphate and silicate of calcium and sodium in pot and field experiments with acid soil, stimulated plant growth. The favorable effect, however, is not yet clearly explained. We may expect from the results of our experiment that the change of solubility of the aluminium compounds brought about by the addition of the salts is one of the main causes of this good effect, the measure of which is the power of the salts to transform the soluble into the insoluble form, though some difference caused by the other factors may exist between the calcium and the sodium compounds.

In order to compare the action of calcium with sodium in practice, we conducted a pot experiment in which acid soil collected from province Kutchan was used. The carbonate, phosphate, biphosphate and silicate of calcium, sodium and potassium were selected for the test. In addition to these the sulfate was tested, its application having been reported to make the soil unfavorable to the plant growth by increasing the amount of soluble aluminium.

Daikuhara (13), and Osugi (35) (36) proved that the soil acidity measured by the potassium chloride method corresponds generally with the quantity of aluminium precipitated by titration with alkali. While this amount of aluminium may not indicate the amount of active aluminium which is toxic to the growth of plants in the soil, it may be expected that the greater the amount of the former, the greater also is the amount of the latter. Then, if this aluminium might be changed into an insoluble form, the amount of toxic aluminium will be decreased. According to this supposition, the equivalent quantity of phosphate, biphosphate, carbonate, silicate and sulfate of calcium, potassium and sodium corresponding to the acidity of the acid soil was calculated as shown in table 3, and was added to the pots each holding 1670 gm. of

the soil, for the purpose of changing the aluminium into insoluble or more soluble forms. The acidity of the soil was measured by the potassium chloride method and it was found to be neutralized by 75 cc. of $0.1N$ NaOH per 100 gm. of the soil.

After the addition of various salts to the soil, 28 seeds of barley were sowed on May 1. On May 18 the growing plants in each pot were thinned to 4 plants of the same growth. The height of the plants was measured on June 15 and 20, and when the barley was harvested on July 28, the length and weight of the plant, the length of the ear and the weight of the seed were measured. Also, the plants were photographed on June 15, and July 28, as shown in plates

TABLE 3

The weight of phosphate, biphosphate, carbonate, silicate and sulfate of calcium, potassium and sodium equivalent to the acidity of 1670 gm. of Kutchan acid mineral soil

POT NUMBER	SALTS USED	WEIGHT OF SALTS
		gm.
1	$CaCO_3$	4.7585
2	$CaHPO_4$	4.3186
3	$CaSiO_3$	5.5198
4	$CaSO_4$	8.1893
5	$CaH_4P_2O_8$	3.7147
6	K_2CO_3	6.5810
7	K_2HPO_4	4.2882
8	K_2SiO_3	7.3614
9	K_2SO_4	8.2998
10	KH_2PO_4	4.3113
11	Na_2CO_3	5.0487
12	$NaHPO_4$	3.7775
13	Na_2SiO_3	7.1736
14	Na_2SO_4	6.7633
15	NaH_2PO_4	3.8093

1 to 3. After the harvest, the acidity of the soil in which the barley had been planted was measured by potassium chloride method, as well as the quantity of aluminium precipitated by titration with alkali. In this case iron was mixed in the aluminium precipitate, but since its amount was quite small, it was not measured, and the total sum of alumina and iron oxide was shown as alumina. The pH value of the soil solution also was measured by Clarke and Lubs method (6). The soil solution used for the determination of H-ion concentration was made by centrifuging the extract from 100 gm. soil to which 200 cc. of water was added. The results are shown in table 4.

The carbonate reduced the acidity of the soil from the original figure of 58.8 to 16.2–26.4 phosphate to 16.8–26.4; biphosphate to 31.6 and silicate 39.6–41.4, but the sulfate had less effect, reducing the acidity only to 46.7–

60.0. As in the case of American soils mentioned by Gillespie (18), and Sharp and Hoagland (48), the pH value of the Kutchan acid soil was very low, but the pH value of the soil solution treated with the various salts appeared to be higher than that of the untreated.   But its change did not correspond with the soil acidity measured by the potassium chloride method.   In the case of phosphate the pH value was 6.0 to 5.9; biphosphate, 6.0 to 5.7; carbonate, 5.9 to 5.6; silicate, 5.9 to 4.9; and sulfate, 5.0 to 4.8.   The order of elevation of the pH value as influenced by the addition of the salts is: phosphate, carbonate,

TABLE 4

Growth of barley in Kutchan acid mineral soil treated with carbonate, phosphate, biphosphate, silicate and sulfate of calcium, potassium or sodium.

NUMBER OF POT	LENGTH OF STEM			TOTAL WEIGHT	LENGTH OF EAR	WEIGHT OF SEED	NUMBER OF CULMS PER POT
	June 15	June 20	July 28	July 28	July 28	July 28	July 28
	cm.	cm.	cm.	gm.	cm.	gm.	
0*	13.3	15.8	30.6	0.50	—	—	4
1	19.7	26.1	52.1	4.00	3.3	1.75	4
2	34.2	44.5	90.0	14.00	7.6	2.25	11
3	12.1	13.9	31.2	1.50	—	—	4
4	15.2	20.4	21.5	1.0	—	—	4
5	34.8	42.1	91.8	13.5	8.7	2.25	11
6	19.4	22.1	44.0	2.25	2.7	1.25	4
7	36.7	38.2	59.8	12.00	6.0	3.25	10
8	32.1	21.8	34.5	2.25	2.3	1.75	4
9	9.1	9.3	9.4	0.25	—	—	4
10	37.6	39.1	80.1·	15.00	8.8	3.35	14
11	19.0	19.7	45.1	2.50	3.6	1.25	4
12	38.4	44.2	79.8	16.00	7.6	2.75	9
13	17.2	21.8	41.8	3.00	3.0	0.75	4
14	11.2	12.6	14.2	0.75	—	—	4
15	38.7	44.3	81.4	15.25	9.9	3.75	9

*Control.

biphosphate, silicate and sulfate, from the standpoint of cation; and sodium, potassium and calcium from the standpoint of anion.

The amount of aluminium precipitated by the titration with alkali nearly coincides with the acidity of the soil except in the case of the addition of sulfate.

The phosphate additions had a good influence upon the growth of the plant.   In spite of its acid nature, biphosphate also caused a marked plant growth.   When carbonate or silicate was added, the growth of barley was better than the untreated, but not as good as with phosphate and biphosphate.

The sulfate-treated pots were rather worse than the untreated, since half or all of the barley in every pot died.   The amount of the culm was greatest in the soil treated with phosphate or biphosphate, followed by the carbonate or silicate-treated pots.   In the case of carbonate, silicate and sulfate the growth of barley was increased with the decrease in the soil acidity.   The acidity of the soil treated with carbonate nearly coincided with that of the phosphate-treated soil while it was lower than in the case of biphosphate.   But the plant growth in the soil treated with the latter two salts was remarkably better than in the soil to which the first had been applied.

TABLE 5

The pH value, the acidity of the soil and the amount of aluminium precipitated by titration with alkali

POT NUMBER	pH VALUE, CLARK AND LUBS METHOD	ACIDITY, POTASSIUM CHLORIDE METHOD	ALUMINIUM PRECIPITATED BY TITRATION WITH ALKALI
			gm.
0	4.2	58.8	0.0362
1	5.6	16.2	0.0100
2	5.9	16.8	0.0117
3	4.9	41.4	0.0275
4	4.8	60.9	0.0467
5	5.3	31.6	0.0217
6	5.8	26.4	0.0162
7	5.9	26.4	0.0171
8	5.3	39.6	0.0249
9	5.1	50.6	0.0403
10	5.8	31.6	0.0220
11	5.9	21.3	0.0140
12	6.0	23.0	0.0149
13	5.5	41.4	0.0265
14	5.0	46.7	0.0373
15	6.0	31.6	0.0220

EXPERIMENT III

From the above it is clear that the addition of phospate or biphosphate to the acid soil was the most favorable for plant growth.   For the purpose of making clear the influence of the phosphate upon the barley in acid soil, further study was conducted.   In this case Kutchan and Tayoro acid mineral soils were used, to which was added 0.1 gm. of nitrogen per pot as the source of nitrogenous plant-food in the form of ammonium sulfate.   In order to avoid the influence of acid liberated from the ammonium sulfate after the ammonia is absorbed by the plant or the soil, calcium carbonate equivalent to the ammonium sulfate also was added.   To one series of the pots, besides the above

two salts, potassium phosphate in an amount corresponding to 0.1 gm. of phosphoric acid was added per pot as the source of phosphatic plant-food, and in the other series it was omitted. Then, to the pots of these two series potassium phosphate, potassium silicate, sodium silicate or calcium carbonate in the amount equivalent to the soil acidity was added, calculated as shown in table 6.

TABLE 6

The weight of the salts added to the soil

POT NUMBER	AMOUNT OF SALTS ADDED AS NUTRIENT PER POT		AMOUNT OF $CaCO_3$ EQUIVALENT TO AMMONIUM-SULFATE ADDED PER POT	SALTS ADDED PER POT EQUIVALENT TO ACIDITY	
	$(NH_4)_2SO_4$	K_2HSO_4		Name	Weight
Kutchan acid mineral soil; 1670 gm. per pot; acidity—75					
	gm.	*gm.*	*gm.*		*gm.*
B1	0.95	—	0.7143	—	—
B2	0.95	—	0.7143	$CaCO_3$	4.7595
B3	0.95	—	0.7143	K_2HPO_4	4.2882
B4	0.95	—	0.7143	K_2SiO_3	7.3614
B5	0.95	—	0.7143	Na_2SiO_3	6.7633
C1	0.95	0.49	0.7143	—	—
C2	0.95	0.49	0.7143	$CaCO_3$	4.7595
C3	0.95	0.49	0.7143	K_2HPO_4	4.2882
C4	0.95	0.49	0.7143	K_2SiO_3	7.3614
C5	0.95	0.49	0.7143	Na_2SiO_3	6.7633
Tayoro acid mineral soil; 1025 gm. per pot; acidity—103.5					
A1	0.95	—	0.7143	—	—
A2	0.95	—	0.7143	$CaCO_3$	5.2256
A3	0.95	—	0.7143	K_2HPO_4	5.7810
A4	0.95	—	0.7143	K_2SiO_3	8.1313
A5	0.95	—	0.7143	Na_2SiO_3	6.9357
B1	0.95	0.49	0.7143	—	—
B2	0.95	0.49	0.7143	$CaCO_3$	5.2256
B3	0.95	0.49	0.7143	K_2HPO_4	5.7810
B4	0.95	0.49	0.7143	K_2SiO_3	8.1313
B5	0.95	0.49	0.7143	Na_2SiO_3	6.9357

After the germination of 28 seeds, 4 plants of barley were retained in each pot of the Kutchan acid soil. In the case of Tayoro acid soil the plants were thinned to 3. The experimental treatment and observation also were the same as in the former experiment.

The results obtained are presented in table 7 and 8, and the relative growths of the plants is shown in plates 4 to 7.

In these experiments, the acidity of the series which received phosphoric acid as plant-food was lower than that of the other series. The acidity of the

soil was decreased in each series when phosphate or carbonate was added, while the rate of decrease caused by the salts was almost similar in the case of Kutchan acid soil but in Tayoro acid soil, carbonate reduced the acidity much more than phosphate.   Silicate also reduced the acidity of the two kinds of

TABLE 7

Growth of barley in Kutchan and Tayoro acid mineral soil treated with sulfate, phosphate, silicate, or carbonate

POT NUMBER	LENGTH OF STEM			TOTAL WEIGHT	LENGTH OF EAR	WEIGHT OF SEED	NUMBER OF CULMS PER POT
	June 15	June 20	July 28	July 28	July 28	July 28	July 28
Kutchan acid mineral soil							
	cm.	*cm.*	*cm.*	*gm.*	*cm.*	*gm.*	
0	13.3	15.8	30.6	0.50	—	—	4
B1	15.1	16.4	30.6	1.25	—	—	4
B2	17.2	17.3	34.4	2.5	2.1	1.25	4
B3	23.3	26.9	50.6	4.75	6.3	1.25	4
B4	18.3	19.1	34.5	1.5	—	—	4
B5	16.9	19.1	30.6	1.0	1.2	0.10	4
C1	17.2	18.8	34.0	1.0	—	—	4
C2	36.4	47.6	87.6	12.5	7.2	3.75	7
C3	47.5	49.1	80.6	24.5	8.7	6.0	12
C4	37.0	45.1	65.4	5.5	6.0	1.75	6
C5	30.0	36.4	53.6	6.5	6.0	0.25	5
Tayoro acid mineral soil							
0	16.1	17.0	27.9	0.5	—	—	3
A1	17.6	19.1	31.0	0.5	—	—	3
A2	30.6	32.4	69.9	9.5	7.5	2.25	3
A3	45.1	58.2	81.8	26.5	9.7	6.25	11
A4	29.9	35.4	53.7	5.5	4.8	1.00	3
A5	31.8	33.0	44.5	6.25	5.4	1.25	3
B1	16.7	19.9	20.3	1.25	3.6	0.25	3
B2	34.2	44.5	77.6	16.0	9.0	2.25	6
B3	45.8	51.6	86.8	35.0	10.5	7.75	15
B4	25.1	36.1	49.6	6.5	6.0	0.5	3
B5	29.7	43.3	51.5	7.5	7.5	0.75	3

acid soil, but its power was lower than that of phosphate.   When ammonium sulfate was added, the acidity was decreased slightly, perhaps because of the excess of calcium carbonate present.

The pH value of Kutchan acid mineral soil was increased by the addition of phosphate.   In Tayoro soil this difference of the pH value was a little greater

than that observed in Kutchan soil. The order of increase of the pH value due to the salts was: phosphate, carbonate and silicate.

The amount of aluminium precipitated by titration with alkali nearly coincided with the acidity of the soil.

The length and weight of stem, the length of ear and also the weight of seed increased in the soil treated with phosphate as a source of phosphatic plant-

TABLE 8

The pH value, the acidity of the soil and the amount of aluminium precipitated by titration with alkali

POT NUMBER	pH VALUE, CLARK AND LUBS METHOD	ACIDITY, POTASSIUM CHLORIDE METHOD	Al_2O_3 PRECIPITATED BY TITRATION WITH ALKALI
Kutchan acid mineral soil			
			gm.
0	4.2	58.8	0.0362
B1	4.8	47.8	0.0344
B2	5.2	20.1	0.0175
B3	5.3	20.7	0.0188
B4	5.0	21.9	0.0185
B5	5.3	37.4	0.0294
C1	5.0	43.2	0.0320
C2	6.0	16.2	0.0125
C3	6.2	16.2	0.0148
C4	5.7	20.1	0.0196
C5	6.0	34.2	0.0274
Tayoro acid mineral soil			
0	3.6	94.5	0.0571
A1	3.6	85.8	0.0607
A2	5.2	16.8	0.0168
A3	5.6	30.0	0.0239
A4	4.1	43.2	0.0331
A5	5.3	49.5	0.0268
B1	3.7	66.7	0.0498
B2	5.3	13.8	0.0147
B3	5.4	23.6	0.0191
B4	4.4	36.8	0.0279
B5	5.3	38.8	0.0306

food, as compared with the untreated while the plants made most marked growth in the soil treated with phosphate for the neutralization of the acidity. Carbonate also promoted the plant growth, followed in order by silicate. But no good result was obtained by the addition of ammonium sulfate and calcium carbonate only.

For the purpose of comparing the effect of various amounts of phosphate upon the growth of the plant, the results obtained with potassium phosphate in second and third experiments are brought together in table 9.

The growth of the plant greatly increased, while the amount of aluminium precipitated and the acidity of the soil were decreased, according to the amount of phosphate given, though the quantitative relation between the amounts was not strictly observed. It is evident at any rate that the plant made a decidedly marked growth from the application of a large amount of phosphate.

According to the results of the first experiment, a small amount of soluble aluminium was retained as insoluble in the soil by the addition of silicate as compared with phosphate, biphosphate and carbonate, although its reaction was more alkaline than that of phosphate and biphosphate. It may, then, be concluded that the poor plant growth in the case of silicate addition in

TABLE 9

The effect of various amounts of potassium phosphate upon plant growth and acidity, and the amount of aluminium precipitated

AMOUNT OF				LENGTH OF STEM	TOTAL WEIGHT OF PLANT	SOIL ACIDITY KCl METHOD	ALUMINIUM PRECIPI- TATED WITH ALKALI Al_2O_3
$(NH_4)_2SO_4$	$CaCO_3$	K_2HPO_4					
		As plant- food	As neutral- izer				
gm.	*gm.*	*gm.*	*gm.*	*cm.*	*gm.*	*cc.*	*gm.*
Control	—	—	—	30.6	0.50	58.8	0.0362
0.96	0.7143	—	—	30.6	1.25	47.8	0.0344
0.96	0.7143	0.49	—	34.0	1.0	43.2	0.0320
0.96	0.7143	—	4.2882	50.6	4.75	20.7	0.0188
—	—	—	4.2882	59.8	6.0	26.4	0.0171
0.96	0.7143	0.49	4.2882	80.6	24.5	16.2	0.0145

experiments II and III, is attributable to the low power of silicate to eliminate soluble aluminium in the soil.

The favorable action of biphosphate, which is acid in nature, also may be explained by the fact that aluminium was retained in the soil as insoluble aluminium phosphate by the application of this salt, as shown in the first experiment, though it did not produce any precipitate of aluminium phosphate from the solution mixed with aluminium chloride and sodium biphosphate. Also the favorable influence of carbonate or phosphate may be explained by the fact that these salts retained in the form of inactive compounds the great amount of toxic aluminium present in the soil.

It is clear from the above that the elimination of active aluminium present in acid soil, is one at least of the favorable factors caused by these salts in plant growth. But, as shown in the pot experiment, the most favorable effect was not given by the chemicals which converted the soluble aluminium into the insoluble in greatest amount. The greatest amount of aluminium was

retained in the case of carbonate, but the plant did not make more marked growth from the application of this salt than with phosphate and biophosphate.

The favorable effect can not be explained, therefore, merely from the standpoint of the power of these salts to change soluble aluminium into insoluble. We must consider other factors.

The low pH value of the acid soil we tested was increased by the addition of the various salts, but the differences did not correspond with the change in soil acidity caused by the addition of the same salts. Though the plant generally made a more favorable growth according to the raising of the pH value of the soil solution, the plant growth and depression of the hydrogen-ion concentration of the soil solution did not strictly coincide. In some cases the plant made a good growth in soil of low pH value, while in others it could not live even under high pH value; hence pH value does not seem to be a great factor causing the unproductivity of acid soils.

The change of the acidity of the soil influenced by the addition of sulfate of calcium or potassium is reported by many authors, for example, Skinner and Beattie (51), Singh (50), Ames and Schollenberger (2), Conner (8), Erdman (16), Lipman (29), and Bear and Salter (3). Some of them observed that the acidity of the soil was increased by the addition of these salts, while others reported the opposite result. In our experiment, when sulfates were added to the acid soil the acidity was generally neither decreased nor increased. Perhaps, such differences found among the results of various authors may be attributed to the difference in the methods used for acidity determination. In some cases true acid was measured; in other cases the amount of aluminium which dissolved out from the soil by the salt added was observed as the acid. A difference also is caused by the amount of sulfate added to the soil, a small amount having no influence, while a large amount of sulfate greatly increases the acidity.

In our experiment the acidity of the soil was not decreased as much by the addition of silicate as we expected, while Conner (10) reported that the acidity was markedly decreased by the addition of dicalcium silicate. The effect of carbonates upon the soil acidity has been widely studied. In Japan Daikubara (14), Sibuya (49), Ishii (27) and others have observed the favorable influence of calcium carbonate for the neutralization of soil acidity. Osugi (35) also obtained good results from calcium and sodium carbonate in treating acid soil. We found the best effect came from the application of carbonate among the salts of the same cation. The decrease in soil acidity resulting from the addition of phosphate and biphosphate also has been thoroughly studied already by Veitch (58), Brook (5), Conner (8), Ames and Schöllenberger (2), Plumber (40) and Mirasol (32). In our experiments also it was found that the depression of soil acidity was brought about by the application of phosphate or biphosphate. The former salt decreased the acidity more than the latter, its degree of depression being almost similar to that of carbonate. The degree of depression caused by biphosphate was found to be greater than that by silicate.

Thus, the order of the depression of acidity brought about by the addition of the salts we tested was: carbonate, phosphate, biphosphate, silicate and sulfate. This order strictly coincides with that of the amount of aluminium retained in the soil by the salts observed in our first experiment. It seems that a certain correlation exists between the change of the acidity (measured by the potassium chloride method) brought about by the application of the salts, and the amount of aluminium converted into insoluble form by the use of these salts. In other words, the soil acidity is responsible to the amount of aluminium which is precipitated by the titration with alkali. Therefore, the salts which convert more aluminium into insoluble form also depress more largely the soil acidity.

As already stated, the plant growth in the soil treated with silicate was poorer than in that receiving phosphate, biphosphate, and carbonate, but better than in the untreated, while the plant in the soil treated with sulfate grew much more poorly than that in untreated. Except in the case of carbonate the growth of the plant depended upon the degree of depression of the soil acidity brought about by the addition of the salts. Though the addition of carbonate caused the greatest depression of acidity, the growth of the plant ranked next to that of phosphate or biphosphate. Then it seems that, though the change of acidity resulting from the use of silicate, carbonate, phosphate and biphosphate is a very important factor in the growth of plants in acid soils, in the case of phosphates it is not the sole factor favorably affecting plant growth.

If the plant growth corresponds with the degree of elimination of toxic aluminium only, caused by the addition of various salts, the soil treated with carbonate should prove most favorable to the plant. On the contrary, the plants have made marked growth in the soil treated with phosphate or biphosphate as compared with carbonate. Conner (10) explained that this inferiority of carbonate to phosphate is due to the solubility of aluminium hydroxide and phosphate in a solution of the same pH value, as hydroxide is dissolved more easily in a weak acid than phosphate. Thus the toxic action of aluminium, appears on the plant in the case of hydroxide more than with phosphate. But in our experiment the amount of aluminium dissolved out in the solution of potassium chloride by the determination of acidity from the soil treated with carbonate, was smaller than in the case of the soils treated with phosphate or biphosphate. This denotes that the more stable aluminium compound was formed in a greater amount in the former than in the latter soils, though the plant made poor growth in the former. We can not believe, therefore, that the difference of solubility of aluminium hydroxide and phosphate is a factor explaining the inferiority of carbonate, as stated by Conner. The good effect of the addition of phosphate or biphosphate might be explained by the special demand of this kind of soil for phosphoric acid as a plant-food. Then, the question arises—If the total amount of soluble phosphate or biphosphate added to the soil is converted into insoluble phosphate, how does it feed the plant?

In many reports it is mentioned that aluminium phosphate can feed plants, though the effect is not great, the salt being relatively insoluble. If this took place in our experiments, a great amount of aluminium phosphate must have been absorbed by the plant in the case of the soil treated with phosphate or biphosphate, for the plants made marked growth. If the opinion developed recently from the view of colloid chemistry is true, that the minute particles are passed through the membrane and absorbed in the plant body (7, 54), it may be that the minute particles of aluminium phosphate present in the soils behaved in this manner. If so, the plant would absorb at the same time with phosphoric acid a large amount of aluminium, which not only is not found in large amount in the plant body, but its existence in a large quantity is very toxic to plant growth. Such a thing, however, can not be considered. Then the utilization of phosphoric acid in such a case should be explained in some other way. Perhaps, a part of the phosphate added may remain in an absorbed form without resulting in the formation of aluminium phosphate, while the other form of phosphate available to plants may be produced by the mutual action of soil constituents with aluminium phosphate. Such phosphates would afford the phosphatic food of the plant in the soil. This phase, of the problem, however, needs further study.

SUMMARY

1. In this paper we have reported the results of our experiments on the behavior of phosphate, biphosphate, carbonate, silicate or sulfate of calcium, sodium and potassium on acid soils in connection with plant growth.

2. The acidity of the soils was reduced by the addition of carbonate, phosphate, biphosphate and silicate of calcium, sodium and potassium in the order mentioned, while sulfate did not make any reduction.

3. The hydrogen-ion concentration of the soil solution also was reduced by the addition of these salts, but the order of the reduction does not coincide with that observed in the case of the acidity.

4. The amount of aluminium dissolved out in the solution of potassium chloride from the soils after the addition of these salts agreed well with that of the acidity. The acidity seems, then, to be due to the amount of aluminium in the solution.

5. In their power to make soluble aluminium into insoluble, the salts rank in the following order: carbonate, phosphate, biphosphate and silicate. Sulfate not only lacks this power, but increases the amount of soluble aluminium. This order well coincides with that of the reduction of acidity by the salts.

6. The growth of barley was affected by the addition of the salts. A favorable effect was produced by phosphate, biphosphate, carbonate and silicate, in the order mentioned; while the unfavorable effect was caused by sulfate.

7. This order seems to agree with that of the salts in converting soluble aluminium into insoluble, except that phosphate and carbonate are inter-

changed. Hence the aluminium abundantly present in acid soils seems to be a very important factor causing inferior plant growth.

8. The superior effect of phosphate upon plant growth seems to be due to the great deficiency of phosphoric acid in this kind of soil.

9. Though the hydrogen-ion concentration of the soil solution also was reduced by the addition of the salts, it did not show any relation to the plant growth.

10. Thus, the inferior quality of the acid soil as a medium for plant growth is due in some measure at least, to the presence of soluble aluminium which is decidedly toxic, and to the deficiency of phosphoric acid.   Hence the chemicals which supply phosphoric acid and cause the elimination of soluble aluminium seem to be the best agents for improving acid soil.

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PLATE 1

FIG. 1. Growth of barley on June 15 in Kutchan acid mineral soil showing the effect of the addition of calcium compounds.

Pot numbers	Treatment
0	Control
1	Calcium carbonate
2	Calcium phosphate
3	Calcium silicate
4	Calcium sulfate
5	Calcium biphosphate

FIG. 2. Growth of barley on June 15 in Kutchan acid mineral soil showing the effect of the addition of potassium compounds.

Pot numbers	Treatment
0	Control
6	Potassium carbonate
7	potassium phosphate
8	Potassium silicate
9	Potassium sulfate
10	Potassium biphosphate

Fig. 1

Fig. 2

PLATE 2

FIG. 1. Growth of barley on June 15 in Kutchan acid mineral soil showing the effect of the addition of sodium compounds.

Pot numbers	Treatment
0	Control
11	Sodium carbonate
12	Sodium phosphate
13	Sodium silicate
14	Sodium sulfate
15	Sodium biphosphate

FIG. 2. Plants shown in plate 1, figure 1, as they appeared on July 28.

MIYAKE, TAMACHI AND KONNO
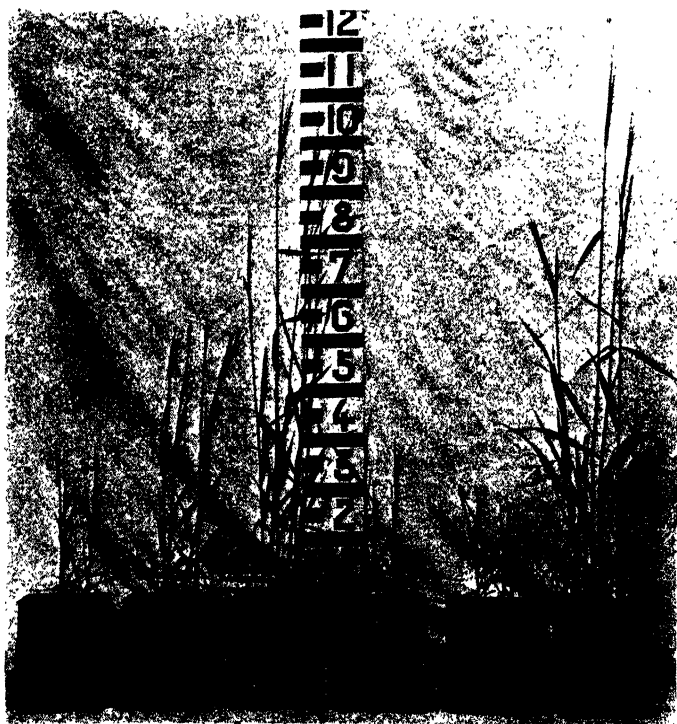
Fig. 1

Fig. 2

Fig. 1. Plants shown in plate 1, figure 2, as they appeared on July 28.
Fig. 2. Plants shown in plate 2, figure 1, as they appeared on July 28.

MIYAKE, TAMACHI AND KONNO
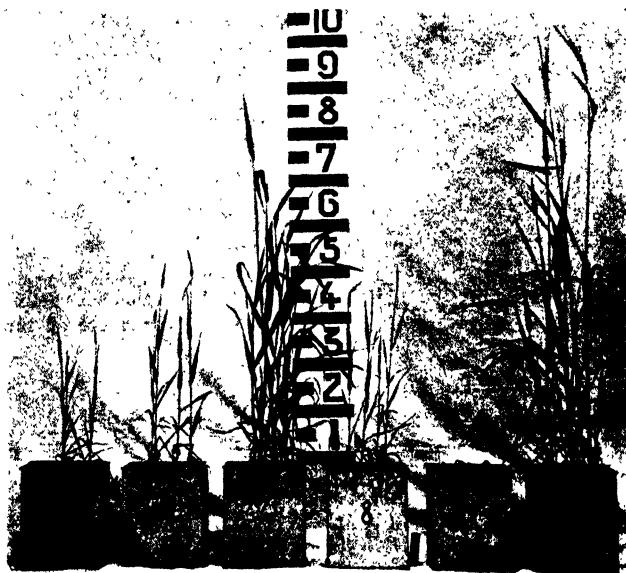
FIG. 1

FIG. 2

PLATE 4

FIG. 1. Growth of barley on June 15 in Kutchan acid mineral soil, with ammonium sulfate and calcium carbonate as sources of plant-food, showing the effect of the addition of various salts.

Pot number	Treatment
0	Control
B1	Ammonium sulfate and calcium carbonate as plant-food
B2	Ammonium sulfate and calcium carbonate as plant-food; with additional calcium carbonate
B3	Ammonium sulfate and calcium carbonate as plant-food; with potassium phosphate
B4	Ammonium sulfate and calcium carbonate as plant-food; with potassium silicate
B5	Ammonium sulfate and calcium carbonate as plant-food; with sodium silicate

FIG. 2. Growth of barley on June 15 in Kutchan acid mineral soil, with ammonium sulfate, calcium carbonate and potassium phosphate as sources of plant-food, showing the effect of the addition of various salts.

Pot number	Treatment
0	Control
C1	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food
C2	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with additional calcium carbonate
C3	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with additional potassium phosphate
C4	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with potassium silicate
C5	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with sodium silicate

Fig. 1

Fig. 2

PLATE 5

FIG. 1. Growth of barley on June 15 in Tayoro acid mineral soil, with ammonium sulfate and calcium carbonate as sources of plant-food, showing the effect of the addition of various salts.

Pot number	Treatment
0	Control
A1	Ammonium sulfate and calcium carbonate as plant-food
A2	Ammonium sulfate and calcium carbonate as plant-food; with additional carbonate
A3	Ammonium sulfate and calcium carbonate as plant-food; with potassium phosphate
A4	Ammonium sulfate and calcium carbonate as plant-food; with potassium silicate
A5	Ammonium sulfate and calcium carbonate as plant-food; with sodium silicate

FIG. 2. Growth of barley on June 15 in Tayoro acid mineral soil, with ammonium sulfate, calcium carbonate and potassium phosphate as sources of plant-food, showing the effect of the addition of various salts.

Pot number	Treatment
0	Control
B1	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food
B2	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with additional calcium carbonate
B3	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with additional potassium phosphate
B4	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with potassium silicate
B5	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with sodium silicate

Fig. 1

Fig. 2

PLATE 6

Fɪɢ. 1. Plants shown in plate 4, figure 1, as they appeared on July 28.
Fɪɢ. 2. Plants shown in plate 4, figure 2, as they appeared on July 28.

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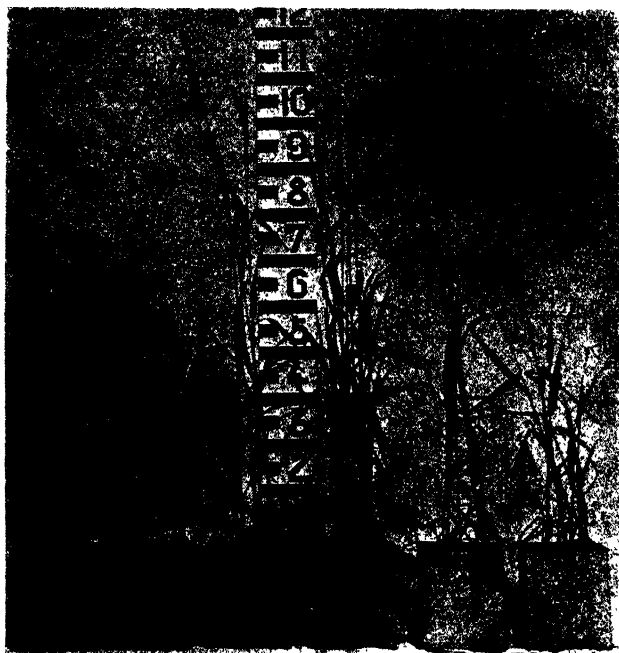
FIG. 1

FIG. 2

PLATE 7

FIG. 1. Plants shown in plate 5, figure 1, as they appeared on July 28.
FIG. 2. Plants shown in plate 5, figure 2, as they appeared on July 28.

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FIG. 1
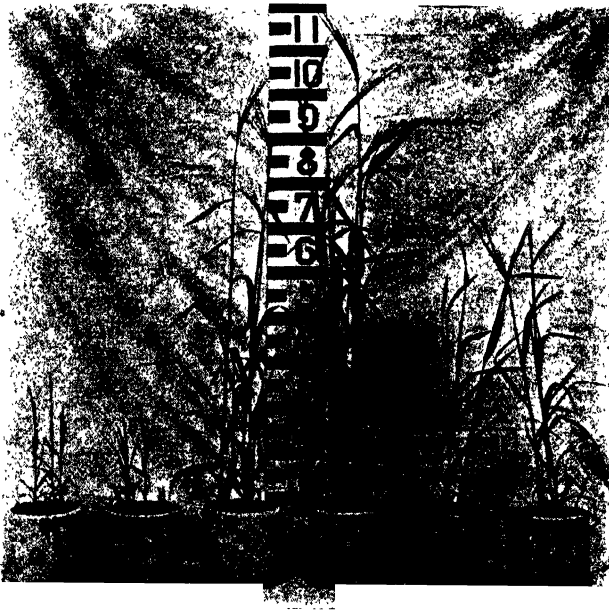
FIG. 2

THE AVAILABILITY OF NITROGEN IN PEAT

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Large deposits of peat which are found at different points on the earth's surface have for many years rendered peat an object of considerable attention as a possible economic source of nitrogen as a fertilizing material and, incidentally also, of organic matter for soil treatment. The literature of the old agricultural chemistry and of soil science is replete with papers discussing experiments with peat or some economic factors connected with its use. In recent years another use for peat has been making demands which have enhanced its economic importance still more. We refer to the use of peat as filler material in commercial fertilizers. Both in the descriptions of some of the experiments to which we have just referred and in the commercial literature it has been repeatedly claimed that peat nitrogen may be regarded as a fairly good substitute for nitrogen in the better known commercial nitrogenous fertilizers. With this situation before us, we started an experiment to test out the availability of nitrogen in peat in a more or less natural condition and in a modified form due to special treatment. This experiment was concluded in 1919, but various circumstances have prevented us from publishing the results until now. In view of the circumstances to which we have alluded above and to the considerable commercial agitation prevalent during the last two or three years in favor of the use of peat for the improvement of the lawns of golf courses and similar places, it seems particularly opportune to discuss the actual results of experiment on this point. None of the other investigations which have a bearing on our experiment have regarded the problem in the way in which we have attacked it and the way in which we have interpreted the results. We append, however, a list of other papers which is of some interest in connection with the material furnished below.

THE PLAN OF OUR EXPERIMENT

Our aim in this investigation was to test the value of peat when applied to a soil which always responds to other nitrogenous fertilizers. Remembering also that the proteins in the peat might be easily hydrolyzed by steam under pressure and by treatment with acid, and possibly on an economical basis, we resolved to compare untreated peat with peat which had been treated

with sulfuric acid, and with peat which had been treated with sulfuric acid and steamed in the autoclave at 25 pounds pressure. The criteria upon which we decided to base our conclusions were the yields of barley in dry matter on the soils treated with the various forms of peat as compared with the yields of barley produced on the same soil which had received high grade nitrogenous fertilizers. The soil used in the experiment was Oakley blow sand which for many years has been shown by our laboratory to be highly responsive to nitrogenous fertilization of all kinds. Whenever peat was added to this soil it was added in quantities which would yield an amount of nitrogen equivalent to that found in an application of 200 pounds of nitrate of soda per acre. The computations made in these applications were based on the area of the exposed soil in the cultures and not on the weight thereof.

The peat which was used was derived from the surface layers of an area of peat land in the delta of the Sacramento and San Joaquin rivers. It was a brownish-black, apparently old material which could be readily reduced by grind'ng to a fairly fine condition. When it was applied to the soil it was very thoroughly mixed with the particles of sand therein. In its air-dried condition the peat contained 1.9 per cent of total nitrogen.

The cultures were grown in the usual glazed earthenware crocks of 2 gallons capacity, five barley plants per crock being planted and harvested. The treatments given the peat were as follows:

I. The peat was treated with sufficient concentrated sulfuric acid to just thoroughly wet it. It was allowed to remain in that condition over night. Enough water was then added to give the peat a content of 50 per cent of water.

II. Some of the acid-treated peat of treatment I. was then submitted to steam pressure in the autoclave at approximately 25 pounds pressure for 3 hours. It was made up to the same water content as the other peat. Five crocks with five barley plants each, as above indicated, were given to every treatment, which were as follows:

1. Oakley sand, no treatment.

2. Oakley sand to which peat had been added in an untreated condition and to an extent sufficient to add the nitrogen equivalent to that in 200 pounds of nitrate of soda per acre for the area in question.

3. Oakley sand to which acid-treated peat had been added on the same basis as regards nitrogen supply as in no. 2.

4. Oakley sand to which had been added steamed acid-treated peat at the same rate as regards nitrogen supply as in the other peat-treated soil.

5. Oakley sand plus nitrate of soda at the rate of 200 pounds per acre.

6. Oakley sand plus sulfate of ammonia at a rate supplying the same quantity of nitrogen as two hundred pounds of nitrate of soda to the acre.

The plants were grown for 100 days in the spring of the year and were harvested on May 21, 1919. The total dry matter was determined after drying for four days at 100°C. The yield from each crock was weighed as a mass. ·

THE RESULTS OF THE EXPERIMENT

Table 1 gives the results obtained with these cultures. It is perfectly clear from even a hasty examination of the dry weights of the barley obtained in the different cultures that an enormous difference obtains between the yields on the nitrate of soda and sulfate of ammonia treated soils and all the others. The nitrate of soda and sulfate of ammonia have induced a marked growth of barley plants as compared with that obtained on the control soils which remained untreated. On the other hand, the yields obtained on the soils treated with the three kinds of peat, prepared as described above, were apparently only slightly greater than those obtained on the control soils

TABLE 1

Dry weights of each group of plants

POT NUMBER	CONTROL		UNTREATED PEAT		ACID PEAT		STEAMED PEAT		NaNO₃		(NH₄)₂SO₄	
	Weight	Devia-tion	Weight	Devia-tion	Weight	Devia-tion	Weight	Devia-tion	Weight	Devia-tion	Weight	Devia-tion
	gm.		*gm.*		*gm.*		*gm.*		*gm.*		*gm.*	
1	1.340	0.340	2.390	0.460	1.950	0.058	1.250	0.512	5.440	0.246	5.230	0.416
2	2.260	0.616	2.300	0.370	1.850	0.158	1.770	0.008	4.810	0.384	5.770	0.124
3	2.000	0.356	1.700	0.230	1.450	0.558	1.090	0.672	4.750	0.444	6.030	0.384
4	1.670	0.026	1.600	0.330	1.590	0.418	1.930	0.168	5.870	0.676	5.520	0.126
5	0.950	0.694	1.660	0.270	3.200	1.192	2.770	1.008	5.100	0.094	5.680	0.034
Mean	1.644	0.399	1.930	0.332	2.008	0.477	1.762	0.474	5.194	0.369	5.646	0.217
Increase over control			17.4%		22.2%		7.2%		216.4%		243.3%	
σ	0.465		0.339		0.621		0.590		0.417		0.265	
Probable error	±0.140		±0.087		±0.187		±0.178		±0.126		±0.080	

which received no treatment. In order to introduce another factor safeguarding the significance of our results more than other experiments on this subject have been safeguarded, we treated our data, so far as such meager replications would allow, by the statistical method. Table 1 indicates not only the actual yield obtained on the several cultures in every series but also gives the deviations from the mean and the probable error involved in all of them.

Before discussing the data from the point of view of the statistical treatment of them, we may point out that the yields of replicate cultures with any given treatment are highly variable. This is particularly true with the cultures of the control soil and of the peat-treated soils. It will be remembered that the treatment of the peat prior to its use in connection with the soils of the experiment could not have produced great abnormalities in the soil, since only a very small quantity of peat was necessary, relatively speaking, to supply the same amount of nitrogen as was contained in a 200-pound

application of nitrate of soda per acre. This, in fact, is supported by the evidence that the acid-treated peat gave slightly superior results to the untreated peat, and both of them apparently gave better results than the control soils. The reason for the poor results obtained with the steamed peat
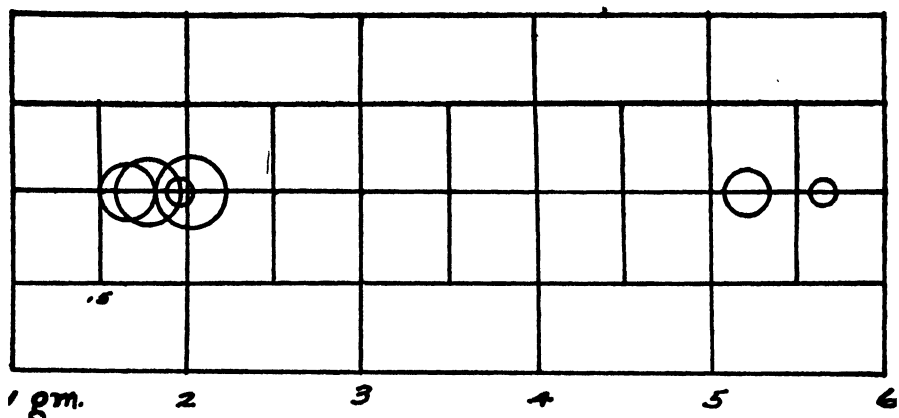
FIG. 1. GRAPHICAL COMPARISON OF ACTUAL YIELDS OF SERIES, MAKING ALLOWANCE FOR THE PROBABLE EXPERIMENTAL ERROR
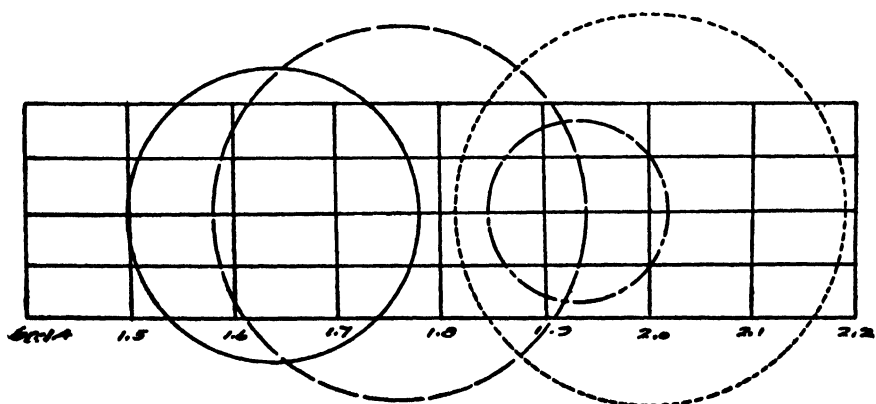
FIG. 2. ENLARGED PORTION OF FIGURE 1, SHOWING RELATIONS OF PEATS AND CONTROL

————————————Control
——— ————Steamed Peat
——— - ————Untreated Peat
— — — — — —Acid Peat

probably lies in the fact that the highly available nitrogen compounds contained in the peat were destroyed by steaming under pressure.

These observations, however, are of little significance when we come to make a statistical study of the data in question. In our statistical studies the reliability of each group of determinations is expressed by the probable

error of the group. This is indicated in table 1. This figure is of such magnitude that the probability of making an error greater than it is equal to probability of making an error less than it, both probabilities, therefore, being one-half. When the data are treated in this fashion it is possible to give a very interesting graphic illustration of their significance. This is given in figures 1 and 2. Figure 2 is particularly illuminating with regard to the problem in hand. The centers of the circles in the figure represent the means of each series. The radii are the probable errors. If any one of the circles representing treated soils overlaps that representing the control soil, the apparent increase in production of the treated series as judged by arithmetical averages, is not significant but falls within the limits of probable error. If, on the other hand, the circles do not overlap, the increase or decrease noted is outside the limits of experimental error and is, therefore, significant. When judged on this basis, the steamed peat treatment gives no increase over the control soils, the acid peat shows an increase of 0.037 gm. per series of five crocks, and the untreated peat a similar gain of 0.059 gm. While both of these figures are significant, they have very little practical interest inasmuch as they represent differences from the control which are too slight to be of any moment in connection with the use of peat for agricultural or commercial purposes. On the other hand, it becomes perfectly clear that the circles drawn on the basis of the sodium nitrate and sulfate of ammonium cultures as given in figure 1, are clearly far outside the reaches of the circle representing the control soil. The differences between the two are, therefore, highly significant.

Two conclusions follow clearly from the foregoing data and discussions. The first is that it makes little difference how peat is treated within economic limits as regards its value as a nitrogen supplying material from the point of view of available nitrogen. Second, no matter how peat is treated, or if it remains untreated, it still is far inferior as a source of available nitrogen to the high grade commercial fertilizer. Third, the intrinsic value of peat as a source of available nitrogen may be said to be almost nil on such a soil as the Oakley sand which responds, however, readily to other nitrogen fertilizers.

CONCLUSION

From the experiment described above, it may be asserted that peat untreated or treated with acid and with acid plus steam under pressure, is of practically no value as a source of available nitrogen when results from particular experiments carried on for this purpose are properly studied.

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INFLUENCE OF SULFUR OXIDATION ON SOLUBILITY OF SOIL MINERALS

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In the semi-arid section of Oregon sulfur is giving excellent results as a fertilizer, especially when used on legumes. According to Powers (4) there are at least 100,000 acres of alfalfa land in Oregon on which the yield can be materially and profitably increased by systematic sulfuring. The increased yield, usually very large, is caused by the lightest applications of sulfur, even as little as 50 pounds per acre yearly. The reason for the phenomenal stimulation in yield is not well understood. Perhaps the sulfur may serve as plant food directly, or bacterial action may be stimulated, plant food may be thrown into solution or other factors may cause the increase.

During the past year, pot studies were started in the laboratory to determine the effect on solubility of essential elements of plant-food, including potassium, phosphorus, and calcium, recognizing that herein might lie in part at least, an explanation.

Two types of soil were used, the one an arid soil called Deschutes sandy loam which is nearly neutral, and the other a soil from the humid section called Willamette silt Loam which is a typical good valley soil but quite acid in reaction. The soils were selected as being expecially adapted to respond to sulfur studies. They were also known to respond to application of potash-bearing fertilizer.

Besides a check, four different rates of sulfur treatment were used, 100, 500, 2500, and 12,500 pounds per 2,000,000 pounds of soils. The pots were maintained at about the optimum moisture content and were sampled three times at intervals of 4, 6 and 9 months. After each sampling, nitrates, water soluble potassium, phosphorus, calcium, and sulfates were determined.

Colormetric and turbidity methods were used throughout the work, following the procedures with some modifications, outlined by the Bureau of Soils (5). While not entirely satisfactory the methods have the advantage of adaptation to small quantities, and suitability for rapid work. In much of this work differences have been sufficiently marked that greater accuracy would hardly be significant.

The results are shown in table 1.

Soluble nitrates determined at each sampling showed that the heavy applications of sulfur depressed nitrification very decidedly at first but to a less extent as time went on.   With an application such as is practical under field conditions there was no appreciable depression of nitrification.

The effect of the sulfur oxidation upon the increase in water soluble calcium was very striking.   The soluble calcium was increased several fold with the heavier applications and even the lightest application of 100 pounds of sulfur produced an appreciable increase in the soluble calcium.   Since legumes and especially alfalfa are heavy lime feeders, this no doubt may be a contributing

TABLE 1

Water soluble plant food in soil treated with sulfur

SULFUR TREATMENTS PER ACRE	N SAMPLINGS			K SAMPLINGS			PO₄ SAMPLINGS			Ca SAMPLINGS			SO₄ SAMPLINGS		
	1*	2*	3*	1	2	3	1	2	3	1	2	3	1	2	3
Deschutes sandy loam															
pounds None	17	10	30	15	14	11	49	50	46	83	67	56	Tr.	15	40
100	18	11	40	18	16	21	47	43	48	118	92	70	125	143	114
500	13	9	26	36	35	40	32	40	38	143	196	208	500	666	714
2,500	Tr.	2	9	67	54	54	23·	31	35	200	370	385	1800	1667	2222
12,500	Tr.	2	4	84	88	98	7	13	27	286	556	833	3000	4167	5555
Willamette silt loam soil (Gouley Experiment Field, Salem)															
None	31	22	21	12	9	11	38	22	28	64	59	66	50	49	53
100	40	22	19	9	9	10	39	20	20	88	92	130	75	137	133
500	33	21	19	15	13	15	31	13	16	125	172	250	135	237	444
2,500	9½	7	9	20	21	29	6	9	9	188	298	769	325	1357	2000
12,500	Tr.	6	5	23	32	48	Tr.	8	18	232	543	1333	400	2853	4000

* 1 Indicates sampling after 4 months; 2, after six months; and 3, after 9 months.

cause for the big response of alfalfa to light sulfur applications.   The continued use of sulfur may cause increased loss of lime by leaching due to the great increase in solubility unless precautions are observed.

Soluble potassium was greatly increased on both soils by the heavier applications.   The oxidation of the sulfur to produce acid amounted virtually to an acid extraction of the soil, with a very dilute acid.   The effect was more marked on the Deschutes soil.   Since arid soils are less deeply weathered, and contain minerals rich in plant food, this result is logical.   The arid soils also being generally alkaline, and changed to acid condition by the oxidation of the sulfur, should give up more plant food to a water extract than would humid soils.   Increased solubility of potassium may be desirable under some conditions but undesirable under others.   When potassium is deficient and

becomes a limiting factor in crop production, the increased solubility should show in increased crop yields. Land left barren, however, would be more likely to lose potassium by leaching after a treatment with sulfur. The general effect should be much the same as from the application of a soluble potassium fertilizer.

The effect of the sulfur on water soluble phosphate was the reverse of the effect upon potassium. The effect was more marked on the Willamette soil, which was made highly acid, since it was already rather acid at the start. This seems to corroborate the oft noted results that acid soils are in need of phosphate fertilizers. The explanation for the reduced amount of soluble phosphate may lie in the fact that increased solubility of the calcium causes the phosphate to be rendered insoluble as tri-calcium phosphate. In any event the solution and reprecipitation of the phosphate as tri-calcium phosphate may not render the phosphorus less available to crops than it was in the original form. If the preponderance of soluble calcium prevents the phosphate from being taken up by iron and aluminum the result may be decidedly beneficial. The depressing effect of the sulfur on the solubility of the phosphate seemed to become less marked at the last sampling. Perhaps in time a redistribution and precipitation of the phosphate may occur, and the depressing effect disappear. On soils, too, with less soluble calcium the effect of depressing soluble phosphate might disappear. This reciprocal relation of soluble calcium relative to phosphate has been noted by other workers (1).

The amount of water soluble sulfates obtained is a rough measure of the rate of oxidation of the sulfur. The Deschutes soil apparently had a low water soluble sulfate content, sufficiently low perhaps that sulfur may become a limiting element of plant food. How general the condition is cannot be stated. The Deschutes soil oxidized sulfur more rapidly, undoubtedly because of its more open structure and partly, perhaps, because of its alkaline or neutral reaction at the beginning. Though there was an increase in the amount of oxidized sulfur with each successive sampling, in no case was nearly all the sulfur oxidized. Though it was four months before samplings were made oxidation probably started almost immediately. Tumbler studies with another soil, Hanford gravelly sandy loam, treated at the rate of 2500 pounds of sulfur per 2,000,000 pounds of soil, showed 6, 13, 23, 47 and 57 per cent oxidized after 1, 2, 3, 4, and 8 weeks respectively. Oregon soils in general according to Halversen and Bollen (2) have an active sulfur oxidizing soil flora.

The oxidation of the larger application of sulfur caused an appreciable increase in the acidity of the soils. The Deschutes soil which was nearly neutral at the start was made very slightly acid at the first sampling with 500 pounds of sulfur. The higher application caused decided acidity. The Willamette soil was made more acid but the acidity of the original soil was so great that the Truog lead acetate test did not give an easily distinguishable difference.

Hydrogen-ion concentrations were determined on both soils at the second sampling only. Results are shown in table 2. The determinations for total lime requirement were made also on the last sampling, and are shown below.

Only the very heavy applications on the Deschutes soil brought the pH value to marked acidity. On the other soil even the lighter applications caused a considerable increase in the hydrogen-ion concentration. Since sulfuric is a very strong acid, a little of it, unless neutralized by some reaction with the soil should produce a marked change in the pH value. The Deschutes soil has a high calcium content and probably contained a number of salts which caused a neutralization of the acid.

The amount of lime as calcium carbonate required to neutralize the acidity is shown for the last sampling as determined by the Jones method (3). The results show that no lime requirement was produced on the Deschutes soil

TABLE 2

Table showing pH values for soils at second sampling and also lime requirement by the Jones method (third sampling)

SULFUR TREATMENT	DESCHUTES SOIL		WILLAMETTE SOIL	
	Lime requirement	pH value	Lime requirement	pH values
pounds	*tons*		*tons*	
0	0	7.0	2.24	6.4
100	0	6.8	2.55	5.4
500	0.32	6.5	2.65	4.6
2,500	1.13	6.3	4.69	4.4
12,500	4.69	4.1	7.54	3.9

with less than 500 pounds of sulfur per acre. On the other soil each application of sulfur increased the lime requirement somewhat. The lime requirements in general ran parallel with the changes in pH values. Alfalfa does best in nutrient solutions having slightly acid reaction, or about pH 6.0. While this plant flourishes in soils of neutral reaction, yet a possible beneficial effect from sulfur applications on arid soil may come about through slight increase in hydrogen-ion concentration.

The physical effect of the sulfur after it was oxidized to the sulfate was very noticeable. The colloidal material which made it very difficult to obtain a clear filtrate was flocculated. The effect was very noticeable for the applications above 500 pounds per acre. The flocculating effect of the sulfate has special significance on heavy soils and on soils where flocculation is necessary in order to wash out harmful accumulations of alkali. In this respect sulfur functions in the same way in the end as an application of gypsum. Sulfur is in three times as concentrated a form as to bulk, and where long freight shipments are necessary may be more economical than gypsum for that reason.

CONCLUSION

The oxidation of sulfur applied to two widely different soils, one representative of arid and the other of humid conditions, caused a decided increase in the water soluble calcium and potassium, but reduced the amount of water soluble phosphorus.

Even the lighter applications produced an increase in acidity, and long continued use of sulfur on soils already slightly acid, would no doubt cause some injury due to acidity, unless neutralized by the use of lime.

The flocculating effect of the oxidized sulfur may be of considerable value under certain conditions.

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THE INFLUENCE OF NITRIFYING BACTERIA ON THE GROWTH OF BARLEY[1]

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The beneficial effect of nitrates for plants is well known, and yet direct evidence, of increased growth of the higher plant while nitrification is in progress is not easy to demonstrate. Owing to the great number of factors involved in the growth of plants, it is sometimes difficult to measure the effect of any one factor. Provided the conditions are proper, nitrification should bring about an increase in the growth of the plant similar to that noted with the nodule bacteria of legumes.

The present report was undertaken for the purpose of measuring the effect of nitrification on growing plants. This work is a part of a major study on nitrification, certain phases of whichwere presented in 1919 and 1921 (1, 2). This paper presents data on the effect of pure cultures of nitrifying bacteria on the growth of barley in sand cultures.

EXPERIMENTAL

The tests were made in 2-gallon earthenware jars containing pure washed sand and a nutrient solution which contained nitrogen in the form of ammonium sulfate. Twelve kilos of sand and 15 gm. of limestone were thoroughly mixed and placed in each jar. These were then sterilized in the autoclave for five hours, and when cool, 20 cc. of the modified Shive's nutrient solution were added. Pure cultures from washed agar of the nitrifying bacteria, *nitrosomonas* and *nitrobacter* were added at the same time as the nutrient solution. The plan is given below.

Group A. Jars 1 and 2, controls, no nitrogen.
Group B. Jars 3 and 4, controls, with nitrogen as ammonium sulfate.
Group C. Jars 5 and 6, nitrifiers with nitrogen as ammonium sulfate.

In the modified Shive's nutrient solution, the calcium nitrate was replaced with an equivalent amount of nitrogen in the form of sulfate of ammonia. The moisture content of sand cultures was made up to two-thirds saturation and kept the same throughout the experiment.

Two weeks later each jar was planted to ten barley seeds which had been treated to remove the bacteria. The plants were thinned to six seedlings per jar. During the growing period, plant food was added from time to time according to the plan. In all, seven applications of the modified plant food were made. To prevent contamination, the jars were kept in a special greenhouse well separated from other plants and only sterilized water used.

The barley grew rapidly except in those jars without nitrogen. At the end of 102 days the plants were photographed and then harvested. The average green weights of the duplicate jars were as follows:

grams

Group A. Control, no nitrogen... 1.5
Group B. Control with ammonium sulfate.............................. 66.5
Group C. Nitrifiers with ammonium sulfate........................... 116.0

The results are striking; the green weights of the plants without nitrifying bacteria are distinctly inferior to those with the nitrifiers. Plate I shows the marked difference in comparative growth of the barley under the different conditions.

A year later a similar experiment was repeated with a slight change. Group A, the controls without nitrogen, were omitted. With this exception the same plan was followed.

Pure cultures of the nitrifying bacteria were added two weeks before planting. At various intervals during the growing period comparisons were made of the plants with nitrifiers and plants without. The presence and the absence of the nitrifying bacteria in the control jars as well as the treated was determined by means of qualitative tests.

It was found that within ten days after planting, the jars receiving the nitrifiers showed a more vigorous growth than those without bacteria. As the plants developed this difference in favor of the inoculated sand cultures became more noticeable. When one month old the plants with nitrifiers were 4 to 5 inches taller than the others and showed much more tillering. Here as in the previous experiment, there were seven applications of plant food, of 20 cc. nutrient solution per jar.

During the growth of the barley of this second test, samples of sand were removed from the jars and tested for nitrates. The samples from jars with ammonium sulfate but no nitrifiers added always gave a negative reaction for nitrates while those with nitrifiers added gave a strong positive test for nitrates.

When 80 days old, the plants were photographed and then harvested. Plate 2 shows the striking difference between the inoculated and uninoculated plants. The average green and dry weights and also total nitrogen content follow:

	WEIGHT OF BARLEY		TOTAL NITROGEN IN BARLEY
	Green	Dry	
	gm.	*gm.*	*gm.*
A. Without nitrifiers added................	145.0	30.0	0.66
B. With nitrifiers added...................	258.0	52.8	0.78

The differences in growth and in total nitrogen are clearly in favor of the jars with nitrifying bacteria present.   The yield of barley in the jars to which the nitrifiers were added was almost twice as much as that in the jars without the culture of nitrifying bacteria.   Under the conditions outlined in these tests it is possible to show by means of plant growth the beneficial effect of the nitrifying bacteria.

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PLATE 1

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PLATE 2

EFFECT OF NITRIFICATION ON GROWING BARLEY

METHODS OF STUDYING THE STRENGTH OF SOIL ACIDS[1]

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The acid properties of a soil depend upon the amount and strength of the acids in the soil. The importance of these two factors, quantity and intensity, in soil acidity has been recognized by many investigators. However, more work has been devoted to a study of the quantity factor than to a study of the intensity factor. The purpose of this investigation was to study and compare methods for measuring the intensity factor in soil acidity.

It is possible to classify soil acidity methods with respect to the influence the quantity and intensity factors have on the results obtained by the method. Classified on this basis the methods would be divided into three groups: first, those which measure the amount of soil acids; second, those which indicate the strength of the soil acids; and third, methods which are influenced by both the amount and the strength of the acids. The first group would include the Veitch, Tacke, McIntire, and various titration methods. The third group includes the Hopkins, Jones, Truog, and a number of other soil acidity tests. Most of the methods in these two groups have been studied and compared by different investigators.

Methods for studying the strength of soil acids have received less attention than the methods of the other two classes. The avidity method of Truog (9) is probably the only one that has been advanced for the specific purpose of studying the strength of the soil acids. Stevenson (8) has used the Tacke method in a study of the activity of soil acids but it is not as well adapted to the purpose as some other methods.

The hydrogen-ion concentration of soil suspensions and extracts indicates the intensity of the acidity of these suspensions and extracts. However, Salter and Morgan (6) and Bradfield (1) have shown that the hydrogen-ion concentration of soil suspensions is influenced by the soil-water ratio. The same condition has been found to be true for the sugar inversion method (5, 6). Consequently these two methods as ordinarily used are not well adapted to the study of the strength of the soil acids. When the procèdure is modified so that the amount of soil acid is a constant the two methods are very satisfactory for a study of the strength of soil acids.

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[1] Published with the permission of the Director of the Alabama Agricultural Experiment Station.

Twenty-five soils representing fifteen soil types were used in this work. The soils were air-dried and passed through a 20-mesh sieve. They were then ground with a rubber pestle to break up the granular structure without grinding the coarse particles.

The strength of the soil acids was determined by three methods: viz., hydrogen-ion concentration, sugar inversion, and by the Truog avidity method. With each of these methods it is necessary to know the amount of acid in the various soils. This was determined by Truog's active acidity method (9) since it is a part of his avidity method. Then for the hydrogen-ion and sugar inversion methods the amount of the different soils was varied so that the amount of acid present would be the same for all soils. In the Truog avidity method the amount of reagent is varied so that it is just equivalent to the amount of soil acid. Hence, all differences obtained by the methods may be attributed to differences in the strength of the acids of the various soils.

The sugar inverting power of soils seems to depend on the amount and strength of the soil acids. Rice and Osugi (5) and Salter and Morgan (6) have shown the influence of the soil-water ratio on sugar inversion. In the determinations reported in this paper the amount of soil was varied so that all samples would contain the same amount of acid. In the case of soils with a high lime requirement a relatively small amount of soil was used. For example, with soil 203, having a lime requirement 15.60 tons per acre, 3.85 gm. of soil was used; and with soil 54, having a lime requirement of 1.15 tons per acre, 52.20 gm. of soil was used. In each case the amount of soil had a lime requirement of 0.06 gm. of calcium carbonate. Therefore, any difference in the amount of sugar inverted by the soils could hardly be attributed to differences in the amount of acid but would apparently be due to differences in the strength of the acid.

The soil was placed in a 300-cc. Erlenmeyer flask with 100 cc. of a 5 per cent sucrose solution and the flask fitted with a reflux condenser. The flasks were then placed in a large thermostat which was maintained at a temperature of 79° to 81°C. for 3 hours. Each flask was shaken by hand every fifteen minutes. After the three-hour period the flasks were cooled, the suspension filtered by suction, and the extract titrated, using Benedict's solution. The results are expressed as milligrams of sucrose inverted by the soil acid.

The results of Salter and Morgan (6) and Bradfield (1) show that the amount of soil acid in a suspension materially influences the hydrogen-ion concentration. Hence, it seemed desirable in this work to vary the amount of soil added to a given quantity of water so that the same amount of acid was present in all cases. Since the results were to be compared with the results of the sugar inversion method the same quantity of soil and water was used for the hydrogen-ion determinations as was used in the sugar inversion method. The measurements were made by the electrometric method, using a Leeds and

Northrup hydrogen-ion potentiometer. The hydrogen-ion concentration was determined before and after heating at 79° to 81°C. for three hours. Heating at this temperature had very little effect on the hydrogen-ion concentration. This is in agreement with the results of Sharp and Hoagland (7). The results in table 1 were obtained after heating and represent the average of closely agreeing duplicate determinations. In most cases duplicates agreed to within pH 0.05.

TABLE 1

The strength of soil acids as indicated by the Truog method, sugar inversion, and the concentration of hydrogen-ions

SOIL NUMBER	SOIL TYPE	LIME REQUIREMENT	AVIDITY BY TRUOG METHOD	SUCROSE INVERTED	HYDROGEN-ION CONCENTRATION
		tons CaCO₃		*mgm.*	*pH*
48	Greenville sandy loam................	2.30	30.9	12.5	6.48
54	Greenville sandy loam...............	1.15	38.7	22.8	6.25
44	Hagerstown silt loam................	2.55	48.6	14.4	5.88
59	Norfolk sandy loam.................	1.20	49.7	40.4	6.15
61	Orangeburg fine sandy loam.........	1.75	53.0	49.6	5.61
186	Ruston fine sandy loam.............	3.55	62.7	24.3	5.73
52	Clarksville silt loam................	3.25	62.7	45.2	5.45
60	Ruston fine sandy loam.............	2.60	67.9	44.4	5.42
104	Norfolk sandy loam.....	2.40	69.5	59.3	5.21
43	Clarksville silt loam................	3.15	72.8	69.1	5.33
101	Louisa fine sandy loam..............	2.75	80.8	64.6	5.23
56	Greenville sandy loam	3.70	84.8	117.2	5.31
666	Norfolk fine sandy loam............	7.50	85.2	68.4	5.23
50	DeKalb fine sandy loam............	2.85	85.5	86.6	5.21
100	Orangeburg sandy loam.............	3.70	85.6	66.8	5.51
45	Holston silt loam.	4.50	87.4	59.3	5.28
97	Louisa fine sandy loam.............	2.95	88.5	88.6	5.16
204	Greenville sandy loam..............	4.90	98.8	60.0	5.28
72	Clarksville silt loam................	2.65	102.0	99.0	5.20
78	Norfolk fine sandy loam............	8.50	110.0	155.1	4.86
77	Susquehanna fine sandy loam........	3.20	110.0	89.0	5.05
47	Oktibbeha clay loam................	3.00	158.0	188.7	4.91
151	Clarksville silt loam................	3.50	210.0	242.0	4.83
197	Susquehanna clay (subsoil)..........	11.50	432.0	293.6	4.93
203	Susquehanna clay (subsoil)..........	15.60	472.0	278.5	4.82

In the Truog avidity method equivalent amounts of soil acid and acetic acid are allowed to compete for a quantity of base just sufficient to neutralize one of the acids. The distribution of the base is determined by titration. The procedure used was the same as that recommended by Truog except for slight modifications to render it more accurate. The time allowed for filtering was made constant for all soils, 2 minutes. The amount of extract recovered from different soils varied slightly depending on the texture. Therefore, a 100-cc. aliquot was titrated and the acidity of the 150-cc. was calculated. It should
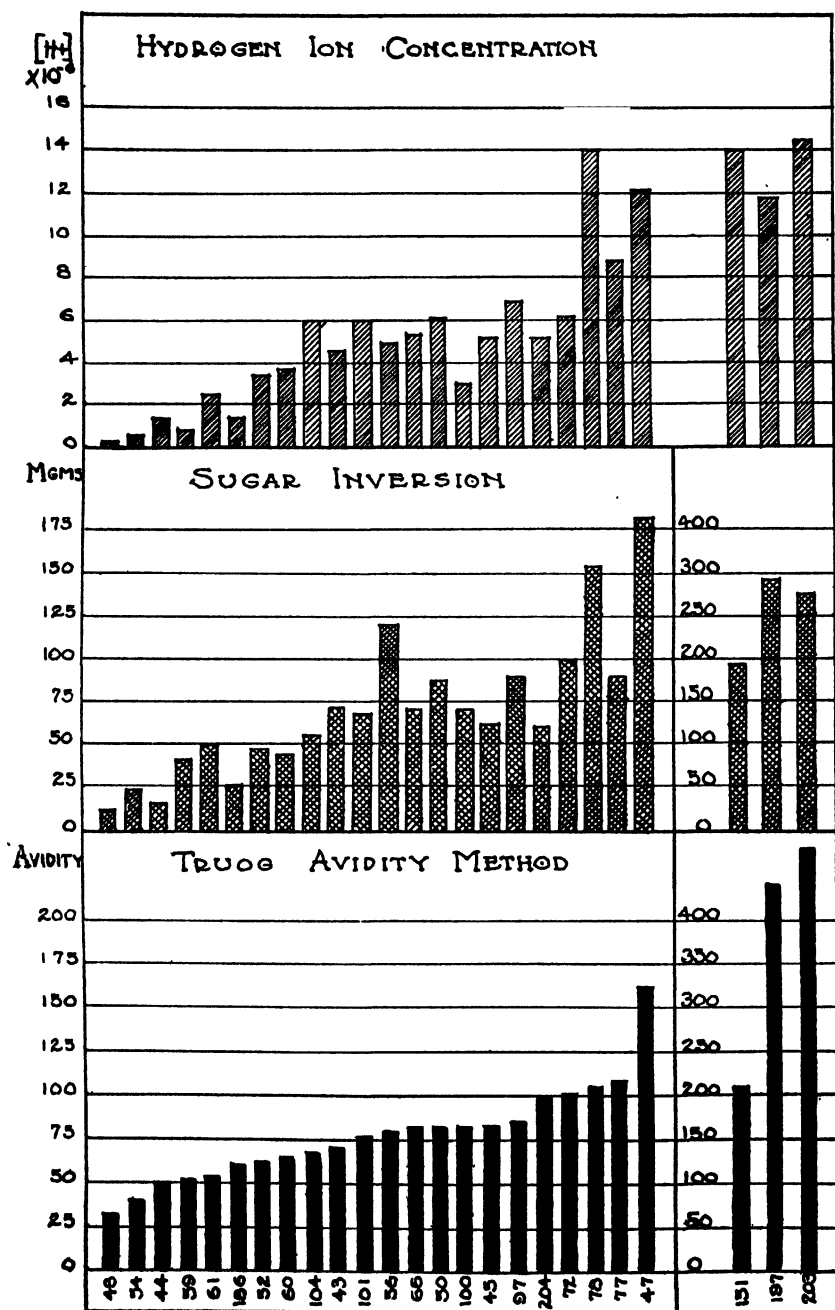
FIG. 1. THE STRENGTH OF THE SOIL ACIDS AS INDICATED BY THE HYDROGEN-ION
CONCENTRATION, SUGAR INVERSION, AND THE TRUOG AVIDITY METHOD

be noted that in this method the amount of potassium acetate added to the soil is exactly equivalent to the acid in the 50-gram soil sample used in the determination.

The results obtained by the three methods are given in table 1. The third column of the table gives the amount of acid in the soil, expressed as tons $CaCO_3$ per acre, as determined by Truog's method for active acidity. The soils are arranged in the order of their avidity according to the Truog method. The hydrogen-ion concentration is given as pH values. The same results are shown graphically in figure 1.

There are several facts of interest regarding the correlation between the results of the three methods. The avidity of the soil acids varied from 30.9 to 472 but sixteen of the twenty-five soils had an avidity between 40 and 100. The amounts of sugar inverted by the soils varied from 12.5 mgm. to 293.6 mgm. and fifteen of the twenty-five soils inverted between 40 and 100 mgm. of sucrose. The hydrogen-ion concentration varied from pH 6.48 to pH 4.82. Seventeen soils gave a pH value between 5.0 and 6.0. These results and a study of figure 1 show that there is a good correlation between the results of the three methods. The coefficient of correlation between the results of the methods was calculated. The coefficients are as follows:

1. Truog avidity and sugar inversion methods.................... 0.899 ± 0.025
2. Truog avidity method and hydrogen-ion concentration.......... 0.789 ± 0.050
3. Sugar inversion method and hydrogen-ion concentration .... 0.817 ± 0.045

All of these coefficients are high, the best correlation being between the sugar inversion and Truog avidity methods.

The fact that the three methods correlate as they do is of special interest when we consider that the principles on which the methods are based differ. Truog's method, based on the competition of acids for potassium, is designed to measure the strength of the relatively insoluble soil acids. The hydrogen-ion concentration is determined by the acids that are in solution and dissociated. The amount of sugar inverted probably depends on the acidity of the solid phase as well as upon the hydrogen-ion concentration of the solution (3, 4). Thus one method is influenced by the acidity of the solid phase, another by the acidity of the solid and liquid phases, and the third by the acidity of the liquid phase only. Since the three methods give similar results with twenty-five soils it is apparent that there must be a close relationship between the acidity of the solid phase and the acidity of the soil solution or extract. This relationship may be explained by the assumption that the acids of the solid phase undergo hydrolysis producing hydrogen ions, and that the extent of hydrolysis is determined by the strength of the acids. No doubt other factors such as the salt content of the solution affects hydrolysis and the hydrogen-ion concentration of soil suspensions. It is probable that if that factor had been constant for the soils used in this study the correlation of the results of the three methods would have been even better.

In the preceding discussion the factors affecting the different methods have been assumed without giving definite proof that they were the only or principal factors involved. There is a little or no doubt regarding the factors influencing the Truog method or the hydrogen-ion concentration. ⸱However, there is some question as to the factors involved in the hydrolysis of sucrose by suspensions of acid soils. A number of investigators have studied the inversion of cane sugar by acid soils with some conflicting results. However, the following facts seem to be well established:

A. Only acid soils, those having a pH value less than 7.0, invert more than very small amounts of sugar (4, 7).

B. Water extracts of acid soils invert sugar (7).

C. Suspensions of acid soils invert considerably more sugar than water extracts of the same soil (5, 7).

D. Increasing the amount of the solid phase in the suspension increases the rate of inversion (5, 6).

Several explanations have been advanced to explain the influence of the solid phase on inversion. Rice and Osugi (5), Osugi (3), and Parker and Bryan (4) attribute the influence directly to the acidity of the acid silicates in the soil. Sharp and Hoagland (7) and Osugi (3) have suggested that it may be due to a higher concentration of hydrogen-ions at the surface of the soil particles than in the solution. Parker and Bryan offered some data which they interpreted as indicating that there was not a concentration of hydrogen ions at the surface of the soil particles. Sharp and Hoagland also suggested that the effect of the solid phase might be due to its stabilizing influence on the reaction of the solution. Salter and Morgan attribute the effect of the amount of the solid phase to the differences in the hydrogen-ion concentrations at the different soil-water ratios. In order to study the influence of the solid phase on the reaction the writers conducted the following experiment.

The object of the experiment was to determine the effect of different amounts of the solid phase on inversion under conditions where the soil-water ratio would have little or no effect on the hydrogen-ion concentration. This was accomplished by using the displaced soil solution instead of water in making the suspensions. A large sample of acid soil was taken from a plot which has received sulfate of ammonia as a source of nitrogen for a number of years. The soil solution was displaced using the procedure of Burd and Martin (2). Sufficient sucrose was added to the displaced solution to make a 5 per cent sugar-soil solution. To 50-cc. portions of this sugar-soil solution were added different quantities of the soil, giving soil-solution ratios varying from 1 to 400 to 1 to 0.78. The suspensions were held at 79° to 81°C. for two hours, shaking by hand every fifteen minutes. After cooling the hydrogen-ion concentration, conductivity and invert sugar were determined. The results are shown in table 2.

An attempt was made to determine the hydrogen-ion concentration by the electrometric method. The results were unsatisfactory probably because of the high nitrate content of the solution and the consequent formation of ammonia at the hydrogen electrode. The reaction of the filtered extracts was then determined colorimetrically. All filtrates were apparently of the same hydrogen-concentration. Theoretically there should be no difference in the hydrogen-ion concentration of the suspensions since the displaced solution had been in equilibrium with the soil for several days when the soil-water ratio was approximately one to one-tenth. The results of the conductivity determinations indicate that the presence of the different amounts of soil had no effect on the cômposition of the solution.

TABLE 2

The sugar hydrolysis velocity constant, hydrogen-ion concentration, and specific resistance of soil suspensions having different soil-soil solution ratios

QUANTITY OF SOIL PER 100 CC. OF SOIL SOLUTION	HYDROGEN-ION CONCENTRATION	SPECIFIC RESISTANCE	SUGAR INVERTED	VELOCITY CONSTANT K
gm.	*pH*	*ohms*	*gm.*	
None	4.0	650	0.189	0.0003207
0.25	4.0	694	0.299	0.0005231
0.50	4.0	710	0.357	0.0006159
1.00	4.0	701	0.438	0.0008454
2.00	4.0	720	0.625	0.0011068
4.00	4.0	717	0.770	0.0013918
8.00	4.0	701	0.990	0.0018361
16.00	4.0	710	1.143	0.0021602
32.00	4.0	694	1.219	0.0023265
128.00	4.0	650	1.390	0.0027110

The results in table 2 show the influence of the solid phase on the rate of inversion of sugar when the hydrogen-ion concentration and conductivity were the same at all soil-solution ratios. It is evident that the solid phase exerts a considerable effect on the rate of inversion. As has been suggested (3, 7), this effect may be due to a concentration of hydrogen-ions at the surface of the soil particles. If there is a concentration at the surface of the particles it seems to depend on the acidity of the particles and might therefore be attributed to chemical forces. Such a hypothesis seems to satisfy many of the phenomena of soil acidity. However, additional investigations will be necessary to determine whether or not this conception of soil acidity is correct. Disregarding the question of the surface concentration of the hydrogen-ions, it seems evident that the rate of inversion is influenced by the acidity of the solid phase as well as by the acids that are in the soil solution.

SUMMARY

The strength of the acids in 25 soils was determined by the Truog avidity method, the sugar inversion method and by the hydrogen-ion concentration.

The last two methods were modified so that the same amount of acid was used in the determination for all soils. The results of the three methods correlate well and this is considered as an indication that the hydrogen-ion concentration of the soil solution is largely determined by the acidity of the acid silicates of the soil.

An experiment was made to determine the effect of the presence of different amounts of soil on the rate of sugar inversion when the specific resistance and hydrogen-ion concentration of the soil suspensions were constant. The presence of the acid soil greatly increased the rate of sugar hydrolysis. The explanation of the influence of the solid phase is not known. It may be due to a higher concentration of hydrogen-ions at the surface of the soil particles than in the solution.[2]

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[2] Additional studies on this problem, made since the manuscript was written, have led the authors to conclude that the explanation of the influence of the solid phase on sugar inversion is as follows: There is a higher concentration of hydrogen-ions at the surface and in the interior of the gel-like aggregates of soil colloids than in the free soil solution. This difference in the hydrogen-ion concentration is readily explained by Donnan's theory of membrane equilibria. The colloids of a mineral acid soil are complex hydrogen aluminum silicates. On hydrolysis these silicates give diffusible hydrogen-ions and non-diffusible silicate ions. According to Donnan's theory the presence of the non-diffusible ion causes an unequal distribution of the diffusible ions. In an acid soil suspension there would be a higher concentration of hydrogen-ions at the surface of the soil particles than in the free soil solution.

The application of Donnan's theory to the study of the system soil—soil solution is of the utmost importance. It is also important that it be considered in a study of the absorption of nutrient salts by plants. Jacques Loeb, "Proteins and the Theory of Colloidal Behavior," presents a clear explanation of Donnan's theory and gives experimental proof of its validity.

A NOTE ON THE PROTOZOAN FAUNA OF THE SOILS OF THE UNITED STATES

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The theory developed by Russell and Hutchinson in 1909 that a "biological factor" is concerned in the characteristic reaction of the microflora of the soil after partial sterilization, has served as the basic stimulus for a tremendous amount of research upon this subject in several different countries. In this, as is well known, the consistent indictment of the protozoan fauna as a factor of prime importance has been most emphatic.

An excellent review of the theories developed previous to, and contemporaneously with that of Russell and Hutchinson has been presented by Kopeloff and Coleman (7) and covers the literature to 1917. In this, they also treat, in a general way, the application of protozoology to the study of the highly complex relations of the microfauna of the soil to the numerous other forms of its microscopic life.

In this question, as in any other of similar nature investigated under widely different conditions, particularly of materials and technique, one finds in the literature certain points of difference that have arisen among the various investigators. Most important among these is that which relates to the actual significance of the presence of a trophic protozoan fauna to the prosperity and efficiency of the bacterial flora. The nature and extent of these controversies and the methods used have been fully reviewed to the date indicated above. It might be noted that American investigators, by no means, have been delinquent in the presentation of data which has seemed strongly controversial to the general theory.

The writer has brought together more than a score of soil samples from widely different points in the United States for the purpose of examining the protozoan fauna according to the methods now in use in the protozoological department, Rothamsted Experiment Station. Each sample was taken by a member of the staff of a state experiment station, placed in a half-pint jar and sealed with a cork-lined, screw-top lid in such a way that the moisture content of the soil as found under field conditions was maintained. In two cases the samples submitted were air-dried. It is a pleasure to thank the workers in the various states for their kind cooperation in the collection of the material. The necessity of taking into consideration the age of the samples and the conditions under which they were held prior to examination is fully emphasized in the in-

terpretation of the results. Particularly for this reason they were studied largely from the qualitative standpoint though a limited number of quantitative examinations were made.

Cutler (2) at Rothamsted has insisted upon the necessity of first gaining some knowledge of the activities and life histories of the soil protozoa before attempting to discover what part they may play in partial sterilization. He has therefore spent sometime in developing standard methods of technique for the counting of protozoa. As a result a method was derived by which it was possible to count the total numbers of the organisms in a soil sample, and further to distinguish between the numbers of active and cystic forms.

Such a differentiation is of prime importance, for it may easily happen that a soil sample may contain large numbers of protozoa the majority of which are in the cystic condition, and unless this is known any conclusions which are drawn relevant to total numbers are almost certain to be erroneous.

This method was given its first extensive application when Cutler, Crump, and Sandon (6) made a daily count of protozoan and bacterial numbers from a described area of "Barnfield." (the classical Root field) through a period of 365 days. This was done in order to discover the relationships between the various members of the soil population under field conditions. The information thus collected upon protozoan as well as bacterial numbers doubtless constitutes the largest body of homogeneous data upon this subject that has been prepared to the present time. With such a mass of data available, it was found practicable to apply statistical methods in its organization and interpretation. By this means certain deductions have been made possible concerning the relations between the periodicity of the bacterial and of protozoan numbers as well as the relation of these fluctuations to changes of season and climate.

An important fact at once evidenced by the investigation was that the numbers of bacteria showed large daily variations, and did not remain constant for long periods of time as had been assumed. Prior to this investigation workers had not hesitated to consider comparable the counts of bacterial numbers in soil samples taken at different periods, sometimes separated by long intervals of time.

Such a procedure is open to grave objections in view of the daily variations that are now known to occur.

The nature and extent of these changes for a single protozoan type compared with bacterial numbers is indicated in figure 1. Here the opposing influence of protozoa to bacteria is well illustrated where Dimastigamoeba and species α either alone or together stand opposite to practically every change in bacterial numbers. According to a contingency table prepared upon the relation of these diverse groups of organisms, the fluctuations in bacterial numbers were found to be explained by the counter tendency of the numbers of these two species of amoeba, acting either alone or together, in eighty-six per cent of the cases. These results would appear to dispose of the earlier

claim as to the existence of the protozoan fauna of the soil in an inactive state and further indicate that, when present, it is of unquestionable significance in its influence upon bacterial numbers.

This view is strengthened by the inoculation experiment of Cutler (3) who was able to reproduce the daily fluctuations in numbers by inoculating sterile
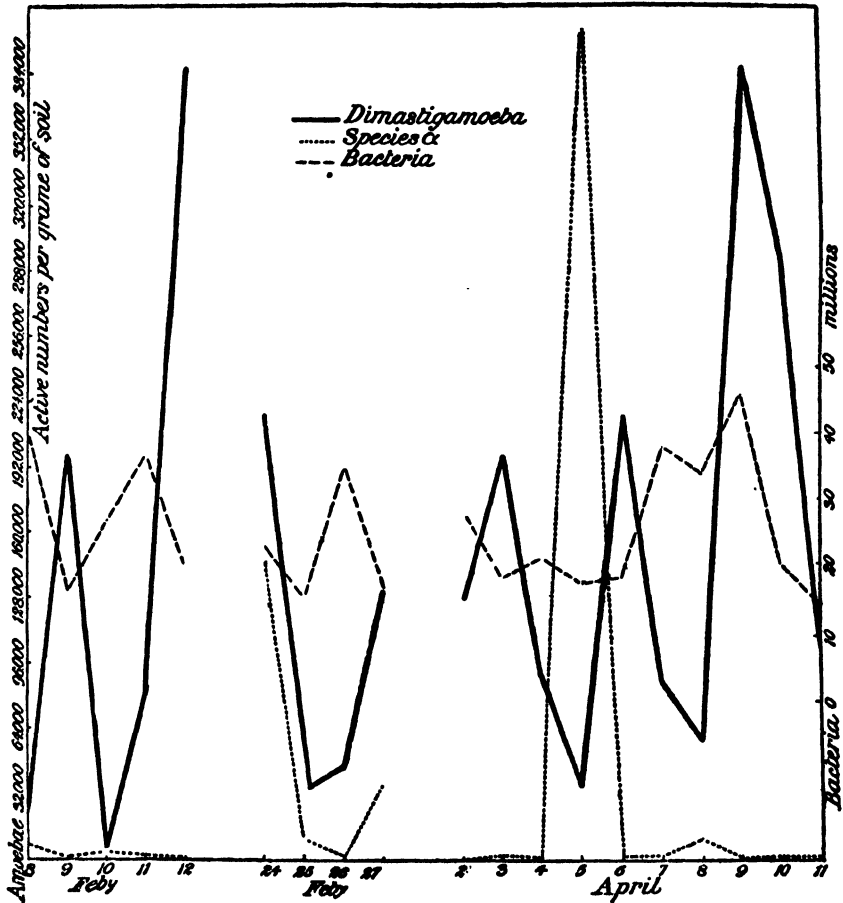
FIG. 1. NUMBERS OF ACTIVE AMOEBAE (DIMASTIGAMOEBA AND SP. α) AND BACTERIA IN 1 GM. OF FIELD SOIL FOR TYPICAL PERIODS IN FEBRUARY AND APRIL
Cutler, Crump and Sandon (6, p. 333)

soil with bacteria and protozoa. In similar soil cultures inoculated with bacteria alone the variations in numbers were not observed.

The violent fluctuations in protozoan numbers that have been observed independent of season under field conditions could not be accounted for by any of the more rigorous climatic changes occurring within the year. This fact has led to studies of the rates of reproduction of individual types in pure

culture under rigidly controlled conditions in the laboratory. These studies, still in progress, reveal results of great interest and disclose a periodicity quite in keeping with that found under field conditions (4,5).

The conclusions arrived at in the more recent work of Waksman and Starkey (8) may be regarded, on the other hand, as representative of the attitude taken by a considerable number of American workers towards the importance of the activity of the protozoan fauna with respect to the biological phenomena that appear consequent to the partial sterilization of the soil. In this work they studied, in part I, samples of Sassafrass loam soil from differently treated plots which, by continuous fertilizer treatment and systematic cropping through some fifteen years, have developed sharp differences in their individual crop-producing power. In part II, they studied a soil of the same type that had been held under uniform conditions of moisture and temperature in the laboratory for more than eleven months and through this treatment had become more or less homogeneous in its physico-chemical balance and constant in so far as the biological equilibrium among the different groups of micro-organisms and their activities was concerned. In part III, the same type of soil as that used above was examined for the ability of its flora to decompose organic substances before and after partial sterilization by different means. In all of this work the influence of various treatments, particularly of different methods of partial sterilization, upon the biological activities occurring in the material under study was interpreted largely upon the basis of careful determinations of evolution of carbon dioxide in conjunction with the progressive transformations of nitrogenous materials as well as the significant changes in numbers in the various broad types of the solid microörganisms.

In the interpretation of the rather considerable data afforded by these studies the authors have concluded that the characteristic effect of "partial steriliza-tion" which was found to appear consistently throughtout the work may be attributed equally well or even better to the activity of the soil fungi and actinomycetes than to protozoa. They regard the fundamental basis of the unusual response of the bacterial flora that follows such soil treatment as existing particularly (a) in the chemical changes in the organic matter of the soil which render it more readily assimilable, (b) in the disturbance of the mic-robiological balance in favor of the development of the bacteria, and (c) in the redistribution of potential food substance formerly existing as protoplasm in the bodies of active organisms of various types but which have been destroyed by the treatment. Upon this basis, the secondary tendencies which follow would be explained largely by the direct competition of the different surviving types for the more or less limited quantity of available food material as well as the fundamental differences among these types in their response to such mate-rials as are available and the variability of their respective efficiencies in the use of such. The diversity of these conclusions particularly as regards the importance of the protozoan factor, will be discussed below.

TABLE 1

Description of soils studied

STATE	SOIL†	REMARKS
Virginia.............	Hagarstown loam	Derived from Dolomitic lime-stone rock
South Dakota.......	Barnes fine sandy loam	"No treatment," plot 140, complete fertility investigations
Illinois..............	Tama or brown silt loam	Common corn belt soil taken from cornfield under cultivation
Indiana.............	Sioux silt loam	From under grass at Experiment Station
Kansas.............	Oswego silt loam	Generally cropped, shale derivation sub-soil hard and impervious
Iowa..............	1. Carrington loam	From Agronomy farm at Experiment Station
	2. Webster silty clay loam	From Agronomy farm at Experiment Station
Colorado...........	(a rather heavy loam)	Section 300, Department of Agronomy, Under rotation of corn, oats, and fallow (1923).
Kentucky...........	Maury silt loam	High phosphatic Trenton Soil. Last crop was corn preceded by clover.
Utah *.............	Greenville loam	Plot 73-G.A., Experiment Station farm. Under culture 40–50 years. Last 10 years received 10 T. manure and 40 in. irrigation water annually.
Tennessee.........	1. Cumberland loam	Cowpea-wheat rotation, unfertilized for 18 years
	2. Cumberland loam	Same soil in cylinders since 1913 with 8 T. hydrated, precipitated $MgCO_3$ per acre
Ohio..............	1. Yellow sand loam	Shallow sandy top soil, moderate organic content. Under grass.
	2. Yellow sandy loam	Subsoil of (1) Yellow sand, no organic matter.
Texas*.............	Lufkin fine sandy loam	Surface soil, College Station
Pennsylvania.......	Hagarstown silt loam	From vegetable garden, heavily fertilized (commercial and farm yard manure)
Massachusetts.......	Merrimac fine, sandy loam	
Minnesota..........	Clarion silt loam	Glacial drift, sub-soil yellow silt, moderately heavy and calcareous. From wheat field.
Wisconsin..........	Miami silt loam	Field plot B. 6 of four-year rotation of clover, corn, oats, wheat. 8 tons manure on corn and 8 tons on wheat
California..........	Dublin clay adobe	Largely alluvial wash from Altamont clay or clay loam. Faculty Club garden

TABLE 1—*Continued*

STATE	SOIL †	REMARKS
Louisiana...........	Loessial silt loam	Continuous corn since 1889. Commercial fertilizer without organic matter to 1908. Cottonseed meal, acid phosphate and 8 tons of manure every three years. Cowpeas turned under with residue every year
Washington.........	Palouse silt loam	Typical wheat soil of east Washington. Rotation, wheat and fallow, residue returned
New Jersey.........	Sassafrass loam	A very light loam with coarse sandy subsoil. Nitrogen availability series at the Experiment Station. Acid phosphate and muriate of potash. In addition: 5A—cow manure 5B—cow manure plus lime 9A—nitrate of soda

* Air dry.

† Most of the samples were taken about the middle of July.

SOURCES AND TYPES OF SOIL STUDIED

The manner in which the soil samples were taken has been indicated above. Most of them were brought over as luggage and a considerable time thus saved in the necessary period which elapsed before their examination. It was thus possible to start working with them promptly upon arrival at the laboratory about August 1. Even so, some of the samples had been sealed a month or longer before the studies which have been recorded were made. In studies here at Rothamsted, the history of the soil, particularly in regard to its manurial treatment, has been found most useful in understanding the diversity of the fauna in soils of different origin. For this reason such information as to type and previous fertilizer treatment and cropping as was submitted with the various samples is presented in table 1. Subsequent reference to these samples in the text will be according to the state from which they were obtained.

QUALITATIVE STUDIES

In the qualitative studies of the samples the practice was to examine them both in hay infusion and upon agar, the latter being prepared in duplicate cultures. Following the preparation and sterilization of the media and its distribution in sterile petri dishes, 5-6 gm. of the moist soil were transferred to each culture by means of a sterile spatula.

The hay infusion was prepared by boiling 50 gm. of chopped hay with one liter of distilled water, filtering and clearing in the usual way with final

TABLE 2

Qualitative studies upon the protozoan fauna of the soil samples described in table 1

SOIL SAMPLE	Cercomonas	Heteromita lens	H. globosus	Sainouron	Oicomonas	Spiromonas	T. spiralis	T. rostratus	Allantion	Colpoda cucullus	Colpoda steinii	Gastrostylus	D. gruberi	Sp. (alpha)	Chlamydophrys	Nudearia
	FLAGELLATA*									FLAGELLATA			RHIZOPODA			
Virginia	+	+	+	+	+	+	+	−	−	+	+	−	+	+	+	−
S. Dakota	+	+	+	+	+	−	−	−	+	+	+	−	+	+	+	+
Illinois	+	+	+	+	+	+	+	+	+	+	+	−	+	+	+	−
Indiana	+	+	+	−	+	+	−	−	+	+	+	−	+	−	−	−
Kansas	+	+	+	−	+	−	+	−	−	+	−	−	+	+	−	+
Iowa 1	+	+	+	−	+	−	−	−	+	+	−	−	+	−	−	−
Iowa 2	+	+	+	+	+	+	+	−	−	+	+	+	+	+	+	−
Colorado	+	+	+	−	+	+	+	+	+	+	+	−	+	+	+	+
Kentucky	+	+	+	−	+	+	+	−	+	+	+	+	+	+	+	+
Utah	+	+	+	+	+	+	−	−	+	+	+	+	+	+	+	−
Tennessee 1	+	+	+	−	+	−	+	−	−	−	+	−	+	+	−	−
Tennessee 2	+	+	+	−	+	+	−	−	−	−	−	−	+	+	−	−
Ohio 1	+	+	+	+	+	+	+	−	+	+	+	−	+	+	+	+
Ohio 2	+	+	+	−	+	−	−	−	−	−	−	−	−	−	−	−
Texas	+	+	+	+	+	+	+	−	−	+	+	+	+	+	+	−
Pennsylvania	+	+	+	+	+	+	+	−	−	+	+	−	+	+	+	−
Massachusetts	+	+	+	+	+	−	+	−	−	+	+	+	+	+	+	+
Minnesota	+	+	+	+	+	+	+	−	+	+	+	+	+	+	−	+
Wisconsin	+	+	+	+	+	+	+	−	+	+	+	−	−	+	−	−
California	+	+	+	+	+	+	−	−	+	+	+	+	+	+	+	−
Louisiana	+	+	+	−	+	+	+	−	+	+	+	+	+	+	−	+
Washington	+	+	+	−	+	−	−	−	−	+	+	+	+	+	−	−
New Jersey	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	−
Total	20	20	20	13	20	15	15	3	13	19	19	10	19	19	13	8
Per cent	100	100	100	65	100	75	75	15	45	95	95	50	95	95	65	40

* The plus sign indicates the presence of the organism concerned in either or both of the media used.

fractional sterilization in the steamer. Before using, this was diluted 50 per cent with sterile tap water. In the case of the solid substratum, ordinary nutrient agar was used with the addition of 1-2 cc. of sterile tap water after introducing the soil. Investigations upon the response of protozoa to variations of reactions in the substratum seem to indicate that practically all types thrive well throughout a considerable range of hydrogen-ion concentration on either side of neutrality.

The cultures were examined at the end of the first and second week and in some cases at the end of the third week. The results of these studies upon the various samples are given in table 2. Only the more common genera of the general groups Flagellata, Ciliata and Rhizopoda are recorded.

For the sake of comparing the population of these samples qualitatively with that of English soils such as have been studied at Rothamsted, it was thought desirable to give particular attention to those types whose numbers have been found significantly high in the extended experiment discussed above. Thus of the samples from twenty different states that were examined, 100 per cent were found to contain *Heteromita* sp., *Cercomonas* sp., and *Oiconomas* sp., 95 per cent were found to contain *Dimastigamoeba gruberi* and Species α, while *Sainouron*[1] (earlier referred to as γ) was found in 65 per cent of the samples. A number of the other forms, particularly of the ciliata, are likewise found to appear in a large proportion of the samples.

Besides those noted in the table, mention might be made of the flagellate *Parapolytoma* sp. found in the Minnesota and California samples and *Actimonas* sp. found in the Ohio sample (top soil) and of the ciliates *Cyclidium* sp. found in the Washington and Massachusetts and *Halteria* noted in the Minnesota sample. Without doubt if all cultures had been examined after four weeks. as well as after two, numerous other forms would have appeared consequent to the disappearance of these noted.

QUANTITATIVE STUDIES

In the study of the samples from a quantitative standpoint Cutler's method described and used in the earlier work in this laboratory was employed. Sufficient of the data obtained upon total numbers will be presented to indicate the nature of the results and demonstrate the method which will be briefly described. As stated above, consideration must be given, particularly in the interpretation of the results, to the treatment of the sample prior to examination.

THE METHOD

The difficulty of separating protozoan cells from the soil mass in which in some way, they are firmly held by the soil particles, has been recognized since the earliest investigations upon this subject. This peculiar power of the soil to

[1] See Sandon, H., 1924, *In* Jour. Linn. Soc., v. 35, p. 449–475.

retain these and other cells has always proved sufficient to render all attempts to make direct counts of the protozoan (1) fauna ineffective. It was for this reason that the method now in use was developed, on the dilution basis.

In the development of a systematic procedure for the routine preparation of soil samples for counting the protozoan fauna by such a method, the prac-

TABLE 3

Number of soil organisms per gram of soil corresponding to the number of negative plates in the three dilution series indicated

From Cutter, Crump, and Sandon (6, p. 341)

1 DILUTIONS 25:102,400		2 DILUTIONS 50:204,800		3 DILUTIONS 50:409,600	
Number of sterile plates	Protozoa per gram	Number of sterile plates	Protozoa per gram	Number of sterile plates	Protozoa per gram
1	110,000	1	220,000	1	420,000
2	59,000	2	118,000	2	230,000
3	36,000	3	72,000	3	140,000
4	23,000	4	46,000	4	95,000
5	16,000	5	32,000	5	64,000
6	11,000	6	22,000	6	44,000
7	7,600	7	15,200	7	30,000
8	5,300	8	10,600	8	21,000
9	3,700	9	7,400	9	15,000
10	2,600	10	5,200	10	10,000
11	1,800	11	3,600	11	7,300
12	1,300	12	2,600	12	5,100
13	900	13	1,800	13	3,600
14	640	14	1,280	14	2,600
15	450	15	900	15	1,800
16	320	16	640	16	1,300
17	230	17	460	17	900
18	160	18	320	18	640
19	110	19	220	19	450
20	79	20	158	20	320
21	56	21	112	21	220
22	38	22	76	22	160
23	25	23	50	23	110
24	15	24	30	24	77
25	6.8	25	13.6	25	51
				26	30
				27	14

tice now in use is so to manipulate the dilution series that for a given soil sample the portion of the soil material carried forward in each successive dilution is always reduced by one-half. The importance of agitating the suspension thoroughly in every instance while withdrawing the sample for dilution is self-evident. In order to make clear the application of table 3, to studies carried out in this manner, the procedure involved is given in some detail.

Ten grams of the moist soil is suspended in 125 cc. of sterile tap-water by shaking vigorously for 3 minutes; 30 cc. of this suspension is then transferred to a sterile water blank containing 30 cc. of tap-water.

After shaking, this same volume is successively transferred in a similar manner onward throughout the series. The first regular transfer from the original suspension thus gives a dilution of 1:25. However if the dilutions are continued through a complete series of 15 transfers in the manner indicated, the final dilution of the original soil sample will be 1:409, 600. It is readily seen that the extent of the dilution for a given sample will depend upon the comparative density of the population to be measured. For a complete enumeration, it is desirable that the dilutions be carried far enough that some 5 or 6 plates, in a continuous series, remain sterile beyond the last one showing the presence of the organisms concerned. In this connection it should be noted that all sterile plates and not merely those at or near the end of the series are systematically enumerated.

From each of the dilutions of a series so prepared, 1 cc. of the suspension is removed to each of duplicate petri dishes containing sterile nutrient agar. Two or three cubic centimeters of sterile tap-water is then added and the plates incubated. Thus, if the dilution series 1:25–1:102,400 (table 3) is adopted and two plates are inoculated from each dilution inclusively according to the procedure indicated, this will furnish a total of 26 plates for examination. Similarly the series 1:50–1:204,800 and 1:50–1:109,600 will require 26 and 28 plates, respectively.

At the time of examination of any series of plates, the total number of plates actually containing the organism or organisms under observation is determined directly with the microscope. Consequently, the density of the population of a definite species in the original sample may be calculated from the number of positive (or negative) plates in a given series. The number of organisms most closely represented by a given number of negative plates in any of the three series of dilutions mentioned above has been calculated by Mr. Fisher, of the statistical department. These data as originally presented by Cutler (6) are given in table 3.

Thus with a knowledge of the number of sterile plates resulting from the preparation of a definite soil sample in the manner indicated above according to any one of these three dilution series, by proper reference to the table, the number of organisms per gram of original sample which this number of sterile plates represents, can be read off directly. Thus if a sample of soil were prepared according to the dilution interval 1:50–1:204,800, and of the 26 plates thereby provided, 9 were found to be sterile of a particular species, it is seen that of this organism there must be some 7400 per gram in the original sample. The number of organisms per gram of moist soil is then converted to its equivalent value for dry material according to the moisture content of the original sample.

As will be seen, the probable error becomes considerably greater as the number of sterile plates approaches either end of a series. In general, a 2-plate difference has not been regarded as significant. Thus by this method a 12-negative plate result with the 1:50–1:204,800 dilution series would represent 2600 organisms per gram of the original sample but this would not be significantly different from a 10-negative or a 14-negative result. Though the probable error by this method, as is seen, is quite high, the results which it yields are distinctly more accurate and consistent than those obtained by any other developed to the present time.

With regard to the differentiation of the active and cystic forms, a method has been developed whereby the cystic forms are counted directly and the active forms thus determined by difference between total and cystic numbers.

TABLE 4*

Quantitative studies upon the protozoan fauna of some of the soil samples described in table 1

SOIL SAMPLE		FLAGELLATES	CILIATES	AMOEBA
New Jersey 5A		4,320	110	960
New Jersey 5A†		10,314	77	1,482
New Jersey 5B†		6,882	...	3,114
New Jersey 9A		2,773	...	340
Washington		1,508	...	96
Iowa No. 2		1,090	...	140
Texas		891	...	128
South Dakota		417	...	22
Wisconsin		1,889	...	421
Tennessee No. 1	Total	200	...	71
	Cystic	15	...	94
Utah	Total	3,180	...	53
	Cystic	3,129	...	53

* Only the total numbers are recorded since in stored soils the numbers of active forms will be entirely different from what would obtain in the field. For a complete and accurate enumeration the use of freshly sampled material is absolutely necessary for each group.

† One month later than first plating of 5A.

In the determination of the cystic forms, the dilution method, as outlined above, is used after first treating the soil sample with 2 per cent hydrochloric acid (sp. gr. 1.15) over night. With soils high in lime, it is necessary to determine first the carbonate present so that the acid may be added in such excess that the final strength will be sufficient to accomplish the desired effect. This treatment has been found to destroy effectively all active forms without injuring the cysts.

RESULTS

With one or two exceptions, all quantitative studies have given results that are surprisingly low in comparison with those obtained from Rothamsted soils. Especially is this true of the ciliates which, with one exception, were

not found in any of the plates though the qualitative studies have shown that with one exception, all contain the two more importants pecies of Colpoda noted.   Only the total numbers for the general groups will be given, with the exception of the Tennessee and Utah samples where the numbers of cystic forms are noted.

In studying the total numbers of protozoa found in the samples in connection with previous treatment of the soil, one finds, even here, rather marked evidence of the stimulating effect of organic matter.   Thus, of the soils of which the previous treatment is definitely known, both 5A and 5B have received liberal applications of cow manure annually (16 tons).   The Utah Soil has received 10 tons per year and the Wisconsin soil an average of 4 tons per year.   On the other hand, as contrasted with 5A, 9A has received essentially the same treatment but its nitrogen for the past fifteen years has been in the form of sodium nitrate rather than as cow manure.   The Tennessee and South Dakota soils, however, have not been fertilized for a considerable number of years.

With regard to cystic forms it was found that the entire population of the Utah soil (previously noted as air dried) appeared to be cystic.   In the Tennessee sample, with normal moisture content, only a few of the flagellates were encysted while apparently all of the amoeba were inactive.

No reliance however, can be placed on the proportion of active to cystic forms in these soils, owing to the abnormal conditions produced by their previous storage.

The fluctuations in numbers between the platings of 5A at different periods are of interest in indicating the possibility of periodicity even in these stored soils.

Since these samples of New Jersey soils are quite identical in type and, in the case of 5A and 9A, in treatment, with those studied by Waksman and Starkey (8, p. 137-156) the results here noted may be found to bear directly upon the conclusions drawn by these investigators.

Waksman and Starkey determined (8, p. 250) the presence or absence of the three general groups of Protozoa in a manner essentially qualitative by introducing 1 cc. of a 1:20 dilution of the soil in a medium of known composition and examining after 5 and 14 days.   Under these circumstances and with the dilution used, infection by any particular type at the time of examination could in no way define an upper limit to the numbers but would only indicate that there must be more than .5 organism per gram of the original material.   On the other hand, sterility in the same instance might define an upper limit to the numbers and indicate that there are probably less than 3-3.5 organisms per gram.   Thus in the absence of quantitative values for the protozoa, the conclusion that this group of organisms is inoperative under the conditions studied would seem to be based largely upon the more positive nature and apparently independent activity of the other groups.   The observed interactivity of these groups is thus presented as a sufficient explanation, from the biological standpoint, for the phenomena observed.

The results of the present studies presented above might be regarded, in a general way, as supporting the counter-protozoa theory held in common by a number of American workers. Thus the current belief that protozoa do not act as a "limiting factor" in normal American soils, particularly under conditions of partial sterilization, as has been frequently concluded, would not necessarily rest upon a lack of the inherent capacity of these organisms to become a "limiting factor" but rather upon their limited number in the soils studied.

It felt however that until careful studies of freshly sampled soils are made upon a basis similar to that presented in this paper, all conclusions drawn in this connection must be regarded as distinctly tentative.

Sincere gratitude is expressed to Sir John Russell for the privilege of conducting these and other investigations in the Rothamsted laboratory; likewise to Mr. D. W. Cutler under whose immediate direction the present studies were carried out in the protozoological department.

SUMMARY

The examination of a series of soil samples from widely divergent points in the United States shows a considerable uniformity in the distribution of the more important of the three protozoan sub-phyla, Flagellates, Ciliates and Rhizopoda. The range of type genera was found to be quite similar to that holding for English soils.

The results obtained from quantitative studies upon these same samples may be taken to indicate, tentatively at least, that a possible explanation of the difference of the conclusions arrived at by English and American investigators may be found in the difference in the extent of the protozoa fauna in the respective materials investigated. Thus the biological phenomena which follow the partial sterilization of the soil and which have been so extensively studied by both groups of investigators, though admittedly similar in nature, may have as their fundamental basis groups of organisms of quite diverse natures.

In the studies presented, the methods now in use in the Rothamsted Protozoological Laboratory have been applied. For the possible service in further investigations of a similar nature these methods have been briefly described.

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THE INFLUENCE OF SODIUM CHLORIDE UPON ALFALFA GROWN IN SOLUTION CULTURES[1]

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INTRODUCTION

The effects of chlorine salts, especially of sodium chloride, upon plants, have been made the subject of study by a number of investigators since the middle of the nineteenth century.

In one of the early volumes of the Journal of the Royal Agricultural Society of England, there is a report by Hannam (21) to the effect that salt increased both the quantity and the quality of the grain of oats, barley and wheat. Good effects of salt applications are recorded by A. Voelker (78) and, years later by J. A Voelker (80, 81), both, on wheat and on mangels. With this last crop there is a uniformity of favorable reports of the effects of sodium chloride, by a number of investigators, such as Gilchrist (20) and others in England, Christensen (14) in Denmark, and Wheeler and Hartwell (86) in this country. Lawes (39) found no difference in yield of wheat, when comparing plots which received salt with those which did not receive it. With barley, Stewart (69) found sodium chloride to have increased the yield of both the straw and the grain.

Experiments with wheat conducted in this country by Shelton (67) at the Kansas Agricultural Experiment Station, showed some increase in grain and in straw, and the production of a cleaner and brighter straw, with salt applications at the rate of 300 pounds per acre. In a later experiment at the same station (19), with oats, a slight decrease was obtained with 150 pounds of salt per acre. Jones (33), experimenting with salt at the rate of 2000, 3000, 5000 and 10,000 pounds per acre, applied broadcast for the purpose of eradicating weeds, found what he calls the "lighter applications," ultimately beneficial to the grass (meadow fescue). All the weeds were killed with the application of 3000 pounds per acre, while the grass grew larger and was of a darker green than on the non-treated, adjoining field.

Lipman and Davis (41) found that salt up to a concentration of 6000 parts per million, stimulated wheat growth.

Beneficial effects of salt are reported by Bolin (9) in case of oats, hay, kohl-rabi, sugar beets and fodder beets. He attributes it to the chlorine.

Stokes (70) observed carrots to have been benefited by salt applications, especially in dry hot seasons.

Sugar beets are another crop which a number of experimenters found to be benefited by salt applications. Briehm (11), the Department of Agriculture and Technical Instruction in Ireland (16), Strohmer, Briehm and Fallada (72), Mette (44), De Ruijter de Wildt et al (17), Schneidewind, Meyer and Munter (63), Bolin (9), Kruger (38), Hoffman (31), and Tottingham (75), all found increased production when salt was applied. In most cases a greater sugar content was also noticed.

Walker (84), and also Rudolfs (60) observed an increased yield of asparagus, with salt applications.

Woods (88, 89) reports an increased yield of turnips but not of oats, potatoes or grass, when treated with salt. In his later experiments, however, he observed that with potatoes, the salt gave a small but uniform increase over the untreated plots.

Stood (71) reports, that water containing one gram salt per liter, is harmful to vegetation. Harris (22) considers chloride in soil as the most toxic of the acid radicals, and sodium as the most toxic of the alkalies.

The germination of peas and other legumionous plants, was found by Jarius (32) to be favored by solutions of 0.4 to 1.0 per cent sodium chloride. Hendry (28) found salt had a harmful effect in sand cultures on cowpeas, Mexican garbanzo, and beans.

At the very beginning of the period when attention was directed, by chemists primarily, to the study of the mineral constituents of the plant, a controversy arose as to the relation of chlorine to plant life. Arendt (2) analysed oat plants and found the chlorine content in the ash of the leaves to be less than in that of the stalks; he was not certain whether chlorine was needed or not. Systematic work on this problem was begun by Nobbe and his co-workers (48, 49, 50, 51, 52). They worked with buckwheat in solution cultures, and as a result of repeated experiments, came to the conclusion that chlorine is essential for the growth of that plant and probably also for that of other plants. Leydecker (40), Beyer (6), Birner and Lucanus (8), and Aschoff (4), confirmed the results of Nobbe, and included a number of other plants among those that need chlorine for their best development. Wagner (83) noticed transitory chlorosis in corn grown in a chlorine-free medium, and that no pollen was formed; but he was uncertain whether to ascribe this to the lack of chlorine. Krauch (37) found that sodium chloride was at least not harmful in solution cultures containing as much as 1 per cent of the salt. Meyer, (45) who made a critical study of the work of the earlier investigators, came to the conclusion that chlorine is needed for buckwheat, but that the quantity needed is very small, and larger amounts may be harmful.

Nobbe's views were opposed most strongly by Knop (35) who denied the essential nature of chlorine in connection with plant growth. Meyer (45), however, pointed out the weakness of Knop's conclusions, mainly on the ground of faulty method in experimentation. Meyer raised the same objections to Aschoff's experiments.

In more recent years, Pfeiffer and Simmermacher (58), who also worked with buckwheat, believe that the existence of a specific need for chlorine has been established, and that the differences of results obtained by the earlier investigators, may be explained by assuming that some plants can do with very little of that element. They show, as Meyer did before them, that buckwheat needs chlorine but in only a very small amount, and may be harmed by larger ones.

The results of a rather extensive investigation by Tottingham (75), show that different plants respond differently to salt treatment: while buckwheat for example, showed a decreased yield, that of carrots and sugar beets was increased. Recent work at the Pennsylvania Agricultural Experiment Station (55) with buckwheat, in washed sand, shows that an increase in dry weight was obtained with salt applications.

Hoagland and Martin (29), working with barley, studied the effect of salts on the intake of inorganic elements and on the buffer system of the plant. From their figures it appears, that with 3000 parts per million of sodium chloride in sand cultures, there was some increase in yield.

The conflicting results obtained in these studies during the last seventy years, and the consequent difference of opinion as to the relation of chlorine salts to plant life, furnish an indication of the complexity of the problem. Some of those investigations, as already pointed out by Meyer (45), suffered from the limitations incident to a lack of knowledge of the proper balance

required to be maintained between the plant nutrients, especially in solution cultures.

Arendt and Knop (3) expressed doubt as to the reliability of the determinations of chlorine in plants. And in fact, it has been repeatedly shown that the analytical data in Wolff's Aschen Analysen, which are of course based upon the earlier determinations, can not always be relied upon, especially with respect to sulfur and chlorine. But even with the improved methods of study at the disposal of investigators to-day, the chlorine question has not reached the stage of definite solution. The effects of sodium chloride, directly and indirectly, in the substratum serving as a medium for plant growth, have been observed to be so multiple and complex, that uniform results should not be expected when different plants or different conditions of the nutrient medium are considered. These effects may be related to the direct action of the salt or its constituent ions, upon plant physiological function; to the action upon other plant nutrients in the medium; to a combination of such activities, as when the sodium of the salt replaces potassium in the plant. The effects may also be related to a physical action exercised by the salt upon the medium, such as the flocculating action on kaolin and on soil noticed by Sachsse and Becker (61).

Nobbe and his associates (48, 49, 50, 51, 52) ascribed to chlorine the rôle of being instrumental in the translocation of starch to the reproductive organs. Meyer (45) concurred in this view but qualified it by saying, that potassium chloride, administered as such, or formed in the salt mixture applied, will perform that function. Aschoff (4) stated that chlorine is probably needed in the building up of each cell. Beyer (6) is of the opinion that chlorine is necessary for seed production.

Interpretations of various kinds have been offered with respect to the effect of sodium chloride on plants grown on soil to which the salt was added. Some of these interpretations are based on observations made upon the behavior of sodium chloride in soil in relation to certain soil constituents or soil conditions.

Voelker (78) explains the good effects of salt applications, as caused by "antiseptic action" which prevents the further decomposition of organic matter and the resulting escape of free ammonia. Peters (56), Frank (18), Eichhorn [cited by Heiden (27)], Beyer (7), Tuxen (76) and Krauch (37), all report, that solutions of sodium chloride extracted a considerably larger amount of mineral and even of organic matter from the soil, than water did. The release of potash was especially noted; but organic matter, sulfur, phosphorus and silica compounds, were also extracted. Eichhorn assumes this to be due to chemical exchange, and suggests that sodium chloride may exchange with soil carbonates, which in turn may act upon even the phosphates of iron and of aluminum, as well as upon the humus. The resulting chlorides of magnesium and of calcium, will again act on the soil, thanks to their pronounced hygroscopic qualities.

Nolte (53) also found that sodium chloride increased the amount of nitrogen, potash and lime in the soil percolate.

From the work of Wheeler (85), Wheeler and Adams (86), Wheeler and Hartwell (87), Hartwell, Wheeler and Pember (24), and Hartwell and Damon (25), which relates to investigations with sodium chloride begun at the Rhode Island Station in 1894 and which was still going on in 1919, it has been established that with some plants, such as beets, radishes, turnips and carrots, sodium can in part take the place of potassium. Increased yield, increased percentage of sodium accompanied by a decreased percentage of potassium, and consequently a better utilization of this element, was brought about by salt applications. Their work also indicates that sodium chloride tends to liberate phosphorus and potassium, and that salt applications may prove of benefit even when full rations of potash are supplied.

Mitscherlich (46) recently asserted that sodium compounds will hinder the formation of difficultly soluble potash compounds in the soil, and thus cause a better utilization of potassium by the plant. Schultze (65, 66) maintains that sodium chloride does not release potassium from potash-zeolites. The plants, according to him, use the sodium as a nutrient, since it may replace potassium to a certain extent. Atterberg (5) experimenting with oats, also comes to the conclusion, that the sodium in sodium chloride may partially replace potassium in the plant. Stood (71) noticed that an increased sodium content is accompanied by a reduction in potash, which fact would likewise indicate a partial replacement of the latter by the former. Suchting (74) similarly noted a depression of the potassium content of potatoes, which received applications of sodium salts. Markwort (43) found that in the case of the sugar beet, sodium applied to the soil, migrates almost completely to the leaves and reduces their potash requirement, thus making available a larger amount for other parts of the plant.

Hoffman (31) found that common salt increased both the quantity and quality of sugar beets, on light as well as on heavy soils, when applications of potash were light and those of sodium chloride heavy. Breazeale (10) observed that plants which have been growing for a period in a medium containing sodium, took up less potash when later transferred to a medium supplied with this element, than did plants which have been growing in a solution containing no sodium.

Voelker (79), and also Kruger (38) are of the opinion that sodium can not replace potassium. In Christensen's (14) experiments, salt caused an increase in the percentage of potassium; he therefore concludes that salt does not assume partly the rôle of potash applications. The chlorine intake was increased more than that of sodium in case of mangolds, and the chlorine, according to him, plays an important part. With potatoes, the salt acted unfavorably, and the chlorine content was increased while that of sodium was not.

Tottingham (75) likewise assumes chlorine to be the active element, and that sodium chloride may act directly as a fertilizer.

In the case of sand cultures, a larger amount of potash was taken up by the barley in the experiments of Hoagland and Martin (29), when sodium chloride was applied at the rate of 3000 parts per million. There was a somewhat greater yield and also a greater percentage of potash in the plants.

Birner and Lucanus (8) state that sodium chloride retards the intake by the plant of lime, sulfur and phosphoric acid, and that it increases the dry matter (in oats) and the quantity of potash and magnesia in the ash.

If the action of sodium chloride in the soil is due to the power of the salt of releasing needed nutrients for the plants, the failure to show any gains with salt applications reported by Lawes (39), may possibly be due to the fact that he applied at the same time an abundance of fertilizers; the salt would in such a case not have an opportunity to assert its effect.

Mette (44) believes the beneficial effects of sodium chloride noted by him, were due to the hygroscopic action of the salt during dry weather.

Den Berger (15) found that sodium chloride may cause puddling, a breaking down of zeolitic materials and changes in volume of soil colloids. Haselhoff (26) also observed chlorides to have injuriously affected the physical composition of the soil, especially that of the loam or clay type. Nolte (53), on the other hand, reports that sodium chloride, the same as sodium nitrate and sodium sulfate, increased the permeability of the soil. Kossovich (36) noted that the sodium chloride hastened the rise of water in a loess clay soil.

Some investigators ascribe the so often noticed superiority of sodium nitrate over ammonium sulfate in fertilizer experiments and practice, as due to the sodium. Schulze (64) found that even in a heavy soil, sodium chloride increased the effect of ammonium sulfate. Briehm (12), also Strohmer and Fallada (73) report that with sugar beets, as good effects were obtained when sodium chloride was applied in combination with ammonium sulfate, as when sodium nitrate alone was applied. Soderbaum (68) however, noticed a benefit with sodium chloride, whether in combination with amonium sulfate or with sodium nitrate, but

not with ammonium chloride. He therefore attributes the good effects to the chlorine. Von Feilitzen (82) could notice no effect of sodium chloride when added to ammonium sulfate. But since he worked with peat soils, it is possible that acidity was a limiting factor, in which case sodium nitrate should prove of greater benefit.

According to Osterhout (54), sodium chloride ions readily penetrate the protoplasm. Reed and Haas (59) present data showing that sodium and chlorine are not absorbed from a sodium chloride solution, as molecular NaCl, but as sodium ions and chloride ions. Christensen, (14) as noted previously, found that the chlorine intake was increased more than that of sodium.

Chittenden and Wachsman (13) state that the activity of diastase is enhanced in the presence of small amounts of sodium chloride.

With wheat in nutrient solutions, Pethybridge (57) observed the leaves to become thinner and to be of a darker green on addition of sodium chloride. Harter (?3), also working with wheat plants, reports, that in a soil containing 0.7 to 1.4 per cent sodium chloride, even if given sufficient water, the plants will immediately after germination assume xerophytic characters. There was a deposit of a waxy bloom on the leaf surface, and a thickening of the cuticle, both of which features tend to lessen transpiration. An increased concentration of the cell sap also took place. When the amount of salt present was not sufficient to cause alteration of structure (with concentrations of 0.06 to 0.08 per cent of sodium chloride in the soil), the transpiration was even increased. Breazeale (10) noticed increased transpiration in presence of sodium even when potash and other minerals were supplied in abundance.

Van Hecke (77) experimenting with fruit trees, found that trees which received 3 pounds of salt were free from gummosis, while the check trees were seriously damaged. He refers to observations made by DeGreffin in Zealand, and by Heime in China, that some fruit trees grown in a soil rich in sodium chloride, did not suffer from gummosis.

Hoffmann (30) studied various salt plants in their relation to sodium chloride, and reported that some sea plants, like *Plantago maritima*, may grow without salt, and that it is only a matter of greater tolerance and not of need, for sodium chloride. The sodium chloride of salt plants may be replaced by potassium chloride. Certain plants, like *Crambe maritima*, show an increased proportion of potassium to sodium, as the distance from the shore, of the locality where they grow, increases. Schimper (62) on the other hand states, that phanerogams which usually live at the sea shore, maintain their chlorophilous habit even when grown on ordinary soil. He also states, that in the case of shore plants, the chlorine is present mostly as sodium chloride, while if grown in places poorer in chlorine, it is mainly in the form of potassium chloride and found chiefly in the leaves.

Jung (34) made up a list of numerous plants which he divides into chlorophilous groups and chlorophobous ones. Leguminosae are not given in any of those groups.

OBJECT OF EXPERIMENT

In a paper published by the writer (42) recently, references was made to the varying chlorine content of alfalfa, and there were also presented the results of an experiment with water cultures that brought out some relationships of that plant to sodium chloride applications. The present investigation comprises a more detailed study of the subject. A greater range of sodium chloride concentrations is covered, the total concentration of the solutions was different from the one used in the previous study, additional phases, such as water absorption and water requirements, were investigated; some details of the experiment were carried out in what might be considered an improved manner, and pot experiments with soil (which will be reported in a separate paper) were also included.

METHOD OF PROCEDURE

Alfalfa seed of the lot used in the previous experiments (42), was used through-out the present work. For germination, the seeds were placed in a spacious crystallizing dish lined with blotting paper, and kept moist with solution "IR2S1." (47), diluted ten times.   On August 20, 1923, two days after sowing, the seedlings were transferred to the germinating net.   This consisted of thinly paraffined mosquito bar stretched tautly over the top of an "agate-ware" pan, 12 inches upper diameter and 3 inches high.   A double net was used.   After the first net was fastened around the pan, a square made of glass rodding 5 mm. in diameter, and reaching almost to the rim of the pan, was laid over it; another net, made up of two thicknesses of mosquito bar, was stretched over the first, the two nets being separated from one another by the thickness of the glass rodding.   The two layers of mosquito bar making up the upper net, were laid together in such a way that the meshes of the one were cut by the threads of the other, thus reducing the size of the meshes of both layers forming the upper net.   This prevented the seedlings from slip-ping through.

On August 29 the plantlets were tranferred to the jars containing the cor-responding solutions, three plants to a jar.   Since duplicate jars were run for each culture, there were six plants for any particular culture solution.   The checks were run in triplicates, giving nine plants for this culture.

The solution known as "R5C2" (Shive), of osmotic value of 1.75 atmospheres, found satisfactory for wheat, and given by the National Research Council (47) as universal control culture in solution culture studies, was here used as check.   The solutions to which sodium chloride was added, were derived from this one, by maintaining in each case the total concentration of the solu-tion as a whole, and the proportions of the three salts, KH_2PO_4, $Ca(NO_3)_2$ and $MgSO_4$, the same as in the check, but substituting sodium chloride, in increments of 0.1 atmosphere, in place of a corresponding osmotic value of the other three salts combined.   This reduction in the osmotic value of the original three salts, was distributed in such a manner, as to leave their initial osmotic proportion undisturbed, varying only their total combined con-centration.

In the present work it was thought preferable to proceed in this way rather than by superimposing the new salt or substituting it for one present in the check.   Superimposing increases the total concentration; substituting the new salt for one present in the check, even when done in osmotic equivalents, disturbs the proportion of the original salts present.   In a solution like that of the present check with a total osmotic concentration of the fairly high value of 1.75 atmospheres, less significant change is likely to be introduced into the medium aside from that caused by the new factor to be studied.   Only the total combined concentration of the original salts is lessened, while the propor-tions in which they are present in the check and the initial total concentration of the solution are maintained.

The respective values of the different solutions used, are given in table 1.

The solutions were renewed every three and one-half days at which time measurements of water absorption were also made; these constituted the partial measurements which at the end were added up to give the total, and from which the water requirements were computed.

Chemically pure salts were used to make up the 0.5 M stock solutions from which the culture solutions were prepared. The sodium chloride was dried to constant weight before being weighed out for the making up of the stock solution.

Iron was supplied in the form of "soluble ferric phosphate," which was made up into a solution containing approximately 0.5 mgm. per cc.. A few drops of this solution were added each time the culture solutions were renewed.

TABLE 1

Partial volume-molecular concentrations and partial osmotic concentrations (in atmospheres), of KH_2PO_4, $Ca(NO_3)_2$, $MgSO_4$ and $NaCl$; also osmotic proportions of KH_2PO_4, $Ca(NO_3)_2$ and $MgSO_4$, in solutions used for the study of the effect of sodium chloride

SOLUTION NUMBER	PARTIAL CONCENTRATIONS							
	Volume—molecular				Osmotic (atmospheres)*			
	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	NaCl	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	NaCl
Check	0.01800	0.0052	0.0150	0.0000	0.875	0.350	0.525	0.000
1	0.01697	0.0049	0.0142	0.00188	0.825	0.330	0.495	0.100
2	0.01594	0.0046	0.0134	0.00376	0.775	0.310	0.465	0.200
3	0.01491	0.0043	0.0126	0.00564	0.725	0.290	0.435	0.300
4	0.01388	0.0040	0.0118	0.00752	0.675	0.270	0.405	0.400
5	0.01285	0.0047	0.0110	0.00940	0.625	0.250	0.375	0.500
6	0.01182	0.0034	0.0102	0.01128	0.575	0.230	0.345	0.600

*In each solution the osmotic proportions of the original three salts are as 5:2:3.

The plants were grown in quart jars for 77 days, and were harvested on November 14, 1923; the tops were separated from the roots at the crown; the drying was done at the temperature of boiling water for 24 hours, at the end of which, the tops and the roots from each jar were weighed separately.

The tops and roots of each jar were ground and analysed separately; the methods of analysis followed, were those of the Association of Official Agricultural Chemists (1).

DISCUSSION OF RESULTS

The data on yield, water absorption, water requirements, nitrogen and chlorine content, are presented separately for tops, roots and for whole plants, in table 2 and in figure 1.

Considering the total yield, in tops and roots combined, it is seen that an increase amounting to 47 per cent over the check taken as 100, was obtained with solution 5, which contained 0.5 atmosphere sodium chloride. An even

TABLE 2

Effect of sodium chloride on yield, water absorption, water requirements, nitrogen and chlorine content of alfalfa grown in solution cultures; average of duplicate cultures; check, average of triplicates

		CHECK SOLUTION: NaCl 0.00, KH₂PO₄ 0.875, Ca(NO₃)₂ 0.350, MgSO₄ 0.525	SOLUTION 1: NaCl 0.100, KH₂PO₄ 0.825, Ca(NO₃)₂ 0.330, MgSO₄ 0.495	SOLUTION 2: NaCl 0.200, KH₂PO₄ 0.775, Ca(NO₃)₂ 0.310, MgSO₄ 0.465	SOLUTION 3: NaCl 0.300, KH₂PO₄ 0.725, Ca(NO₃)₂ 0.290, MgSO₄ 0.435	SOLUTION 4: NaCl 0.400, KH₂PO₄ 0.675, Ca(NO₃)₂ 0.270, MgSO₄ 0.405	SOLUTION 5: NaCl 0.500, KH₂PO₄ 0.625, Ca(NO₃)₂ 0.250, MgSO₄ 0.375	SOLUTION 6: NaCl 0.600, KH₂PO₄ 0.575, Ca(NO₃)₂ 0.230, MgSO₄ 0.345
Dry weight, grams	Tops	3.895	4.499	3.849	4.826	3.238	6.208	4.797
	Roots	1.352	1.534	1.337	1.583	1.247	1.545	1.393
	Whole plants	5.247	6.033	5.186	6.409	4.485	7.753	6.190
Relative dry weights	Tops	100.00	115.51	98.82	123.9	83.1	159.4	123.2
	Roots	100.00	113.46	98.89	117.0	92.2	114.3	103.0
	Whole plants	100.00	114.99	98.84	122.1	85.5	147.8	117.9
Water absorption, cc.		2,227	2,532	2,208	2,659	1,993	3,283	2,546
Water requirement, cc.	Tops	576.6	562.0	574.0	556.8	622.3	529.9	544.2
	Roots	1,652.6	1,643.0	1,674.2	1,625.0	1,598.0	2,117.0	1,839.0
	Whole plants	426.6	418.6	426.8	412.2	447.3	421.9	419.5
Nitrogen content, per cent	Tops	3.38	3.45	3.15	3.29	3.52	3.18	3.43
	Roots	3.03	2.75	2.50	3.02	2.56	2.80	2.89
	Whole plants	3.29	3.27	2.98	3.21	3.25	3.10	3.31
Chlorine content, per cent	Tops	0.04	0.21	0.36	0.37	0.66	0.63	0.80
	Roots	0.04	0.18	0.24	0.29	0.43	0.53	0.86
	Whole plants	0.04	0.20	0.33	0.35	0.60	0.61	0.81

FIG. 1. GRAPHIC SUMMARY OF DATA DETERMINED

higher relative increase of tops, namely, 59 per cent, was produced by this solution. The relative increase in roots was 14 per cent, which is slightly below the highest relative increase in roots produced by solution 3, with 0.3 atmosphere sodium chloride. Solution 3 produced the next highest relative increases, 23.9 and 22 per cent of tops and whole plants, respectively, over the corresponding values of the check. Solution 6, which received 0.6 atmosphere sodium chloride, is third in order of increase over check with respect to whole plant yield, the value of this increase being 18 per cent; the value for the increase in tops, however, is substantially the same as that of solution 3. Solution 1, with 0.1 atmosphere sodium chloride, produced a relative increase over the check of 15 per cent each for tops and whole plants, and a somewhat slighter increase, 13 per cent, for the roots. Solution 2, with 0.2 atmosphere sodium chloride, showed a slight relative decrease of about 1 per cent for tops, roots and whole plants, as compared with the check. A significant relative decrease was shown by one solution out of the six containing sodium chloride.

TABLE 3

Comparison of values for water absorption in relation to yield of whole plant found, with those calculated on the basis of water absorption relative to yield of whole plant of check

SOLUTION NUMBER	YIELD (WHOLE PLANT)	WATER ABSORPTION		DIFFERENCE
		Found	Calculated	
		cc.	*cc.*	*per cent*
Check	100.0	2,227		
1	115.0	2,532	2,560	−1.1
2	98.8	2,208	2,200	−0.4
3	122.1	2,659	2,719	−2.2
4	85.5	1,993	1,904	+4.5
5	147.8	3,283	3,291	−0.3
6	117.9	2,546	2,625	−3.0

This was solution 4, with 0.4 atmosphere of that salt. In this case, the values for tops, roots and whole plants, as compared with the check taken as 100, were 83, 92 and 85 respctively, a relative decrease for the whole plant of 15 per cent.

The greatest relative increases occurred in the yield of tops; this is worth nothing, since in the literature dealing with this subject it is often emphasized that the roots are affected to a great extent.

The curve for water absorption, it will be observed, follows the direction of those for yields of tops and whole plant. The greatest quantity of water absorbed, took place from culture 5, which produced the greatest yield. The water absorption by the plants in the other solutions, followed closely the order of yield of whole plant. This is brought out more clearly in table 3 in which, for comparison, are given the actual figures for water absorption by the plants in the different solutions and a corresponding set of figures calculated by using the yield of whole plant and water absorption of the check as a basis. From

the column giving the differences, in per cent, between the amount calculated and the amount found, a very close approximation is shown to exist between the two sets of figures.   It would therefore seem, that with solutions of the type here used, water absorption is a direct function of yield of whole plant for alfalfa, at least during the first 11 weeks.

The values for water requirements, do not show much variation, if whole plant yields are considered.   This was to be expected, after the relationship which has just been shown to exist between water absorption and yield of whole plant.   It is only with solution 4, which produced the lowest yield, that the water requirement runs up to 447 cc., as against 426 cc. of the check. The differences between the other cultures, expressed in per cent, and the check, range from 0.0 to 3.5.   When comparison is made between the water requirements for the yields of tops of the different solutions, more pronounced differences are encountered.   Here we find the lowest value, 530, for solution 5 which produced the highest top yield, and the highest value, 622, for solution 4, with the lowest yield of tops.   The reverse relationship applies to the roots of these respective solutions, the values being 2117 and 1598 for solutions 5 and 4, respectively.   This would indicate, that where the total yield was low the ratio of root growth to that of tops, was greater than where the total yield was high.   In the two extreme cases of cultures 4 and 5 which respectively represent the lowest and highest yield, the root yields were respectively 28 and 20 per cent of the total.   .

The percentages of nitrogen in the plant as a whole, do not show variations of a magnitude to indicate any definite relationship between this criterion and that of any of the others studied.   In all solutions except solution 3, the roots show a larger percentage of nitrogen than that present in the roots of the plants from the check culture.   Of the nitrogen percentage in tops, culture 5, with the highest yield, gave tops with a value of 3.18, substantially the same as the lowest value for nitrogen percentage of tops in any of the seven cultures studied.   Culture 4, with the lowest yield, contained 3.52 per cent nitrogen in tops, which was the highest value for any of the seven cultures. But, considered in the light of the usually prevalent variations in the nitrogen content of even the same kind of plants grown under what appears to be the same conditions, the differences here noted cannot, without further investigation be taken to indicate the existence of a clearly defined relationship between the the nitrogen content and any other criterion of growth here considered.

In the previous preliminary study (42) on the effect of sodium chloride on alfalfa referred to, it was found that the chlorine intake of the plant in the different solutions, varied directly with the amount of sodium chloride supplied, and that this held good for the roots as well as for the tops.   The roots, however, had a considerably smaller percentage of chlorine than the tops.   Similar results were obtained in the present study up the limit of the range of sodium chloride applications tested.   And since the range here covered was 0.2 atmosphere higher than the one previously studied, and considering further that the

total concentration of the solutions in the present investigation was 1.75 atmospheres, or 0.75 atmosphere higher than the total concentration previously used, it would seem justifiable to conclude from the similarity of results obtained under the two different conditions that alfalfa in solution cultures supplied with sodium chloride, will, within the limits tested, take up an increasingly larger amount of chlorine with the amount of sodium chloride supplied.

With respect to yields, the results of the present study likewise approach those obtained in the earlier one: an increase in yield usually being produced by the solutions containing sodium chloride.   ·

The observation made in connection with the previous study, that no evidence was found of any relationship between the nitrogen content of the plants from the different solutions, and any other criteria of plant measurements, was found to apply also to the results obtained in the present study.

There is likely to be difference of opinion as to whether, in consideration of the fact that the sodium chloride also caused yield increases, the salt acts as a stimulant or as a mineral nutrient for the alfalfa plant. As yet no well defined distinction has been established between the terms "stimulant" and nutrient." It would appear, however, that the term "stimulant," in connection with chemical elements taken up by the plant, should be restricted to denote a substance which, when present in the medium, enhances growth without necessarily being absorbed by the plant in any significant quantity. At any rate, the amount taken up may not at all bear a direct relation to that supplied. With such tentative distinction in mind, and making due allowance for the various effects that sodium chloride may exercise when applied to the soil, it may not be improper to assume, that the sodium chloride here supplied to the alfalfa in solution cultures, acted as a mineral nutrient, which helped materially towards a better development of the plant.

SUMMARY AND CONCLUSIONS

1. Alfalfa was grown for 77 days in solutions with amounts of sodium chloride varying from 0.0 to 0.6 atmosphere osmotic pressure; Shive's solutions R5C2 (1.75 atm.) being used as check.

2. An increase in yield over the check was observed in five out of the six cultures containing sodium chloride.

3. The greatest relative increase occurred in the yield of tops.

4. The curve for water absorption followed the direction of the curves for yields of tops and for those of whole plants.

5. Not much variation was noticed in the values for water requirement, when whole plant yields are considered.

6. More pronounced differences were found when the values for the water requirements of tops are compared. The lowest value, 530 corresponds to the cultures with the highest top yield, while the highest value, 622, resulted with the culture producing the lowest yield of tops.

7. There is an indication, that the ratio of root growth to that of tops, is greater where total yield was low than where total yield was high.

8. The variations in the nitrogen percentages of the whole plants, were not of an order to indicate with certainty any definite relationship between this datum and any of the others studied. The roots from the sodium chloride cultures show a larger nitrogen percentage than those from the check cultures.

9. The chlorine intake of the plants varied directly with the amount of sodium chloride supplied. This applies to the roots as well as to the tops. The roots however containing a much smaller percentage than the tops.

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PHOTO SHOWING THE METHOD OF GROWING ALFALFA SEEDLINGS

NOTES ON A METHOD FOR THE DETERMINATION OF SULFUR IN SOIL

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Within recent years, the question of sulfur as a factor in soil fertility has assumed considerable importance. With the growth of interest in the question, several experiment stations have made sulfur determinations of their soils. Strangely enough up to the present time, there has been no satisfactory method for the purpose. The so-called "official" method of the Association of Official Agricultural Chemists, as adopted in 1907 (4) was recently taken off the "official" list, and placed into the "tentative" class (5). Realizing that the method was very unsatisfactory, the Association in 1919 appointed a referee on methods for the determination of sulfur in soils. The referee reported on his work in 1920 (1) and again in 1921 (2).

Notwithstanding the considerable amount of work done by the referee and his associates in coöperation with various experiment stations, the method thus evolved failed to satisfy the referee, who recommends a further study of methods. Six different methods of bringing the sulfur into soluble form were studied by the referee; viz. (1) sodium peroxide combustion, (2) magnesium nitrate combustion, (3) aqua regia digestion, (4) nitric acid digestion, (5) combustion with a mixture of magnesium nitrate, calcium carbonate, and ammonium chloride, and (6) calcium peroxide combustion.

In every one of these methods, soil charges of 10 to 25 gm. were used. Correspondingly large amounts of reagents had to be used, which in turn necessitated the employment of large-sized glassware. All this makes the methods rather cumbersome and time consuming.

Previous to precipitation of the sulfur, iron and aluminum are precipitated, which operation introduces a very undesirable feature. Precipitates iron and aluminum hydroxides have a large capacity for absorption of sulfates, and successful washing of sulfates from these hydroxides is an exceedingly difficult task.

OLSON'S METHOD OF SULFUR DETERMINATION IN SOIL

In the evolution of a method for sulfur determination in soils, the Olson's modification (3) is a step in the right direction. The Olson's method (3, p. 7-11), in substance, is as follows:

Two grams of soil, 10 to 12 gm. sodium peroxide, 0.5 gm. sugar, and 1 gm. of a finely ground mixture consisting of 5 parts of boric acid, 4 parts of sodium nitrate, and 1 part of metallic magnesium, are placed in a Parr electric sulfur bomb. The ingredients are thoroughly mixed, and the charge is exploded with the bomb under water. The charge is taken up with water or acid, and dehydrated from one to three times to remove silica. The precipitation with barium chloride is made in the cold and in the presence of iron and aluminum. Olson states (3, p 9) that it was found preferable to "add 10 cc. of 10 per cent cold barium chloride slowly and evenly on the surface of cold liquid, which has first been neutralized with ammonium hydroxide and then slightly acidified with from five to six drops of concentrated HCl. Upon standing twelve or more hours, the mixture of sulfates and barium chloride is thoroughly stirred, after which it is allowed to stand at least until the barium sulfate has nearly, if not entirely, settled.

Olson's method has several distinct advantages in comparison with the old procedure adhered to by the Association of Official Agricultural Chemists, or those recently proposed by its referee. In the first place, in precipitating sulfur in the presence of iron and aluminum, it avoids the danger of losing some sulfur in absorption by iron hydroxide. In the second place, it deals with a small amount of soil, thus permitting the operation to be carried out in smaller containers. This point, however, is carried too far for the best results. In the third place, in exploding the soil mass in the Parr's bomb, the disintegration of soil and oxidation of sulfur are unquestionably complete.

A PROPOSED MODIFICATION OF METHOD FOR SULFUR DETERMINATION IN SOIL

In taking up the systematic sulfur determination of Illinois soils in connection with the soil survey of the state, several methods were tried in this laboratory. A modification of Olson's method was finally adopted that with three years of usage has proved to be shortest in operation and among the most reliable in the results obtained, as compared with any method that has come under the writer's observation.[1] This modification allows the use of a somewhat larger soil sample, permits employment of a simpler and less expensive bomb for the disintegration of the soil, simplifies the accelerating agent, and shortens the procedure by eliminating a second dehydration of silica and by making a neutralization by ammonia unnecessary.

The modification, as adopted in this laboratory, is presented herewith:

Three grams of soil (0.5–1.5 gm. of peat or muck) are mixed with 0.5 gm. of powdered magnesium (to start the combustion) and 10 to 15 gm. of sodium peroxide in a Parr heat ignition bomb. The bomb is closed, and the contents are exploded by heating the bomb moderately over the free flame of a Bunsen burner. The bomb is cooled by setting it in cold running water, covering three-fourths of its height. The fusion is washed with hot water from the bomb into a 400-cc. beaker, neutralized with 1:1 HCl; an excess of HCl is added and the solution evaporated on a water or steam bath until the silica is thoroughly dehydrated. From 24 to 48 hours is usually required for evaporation and drying. The residue is taken up with 10 or 15 cc. 1:1 HCl, the beaker is covered with a watch glass, and

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heated on a steam bath for 5 or 10 minutes. The moistened material is diluted with about 100 cc. hot water, washing the sides of the beaker and stirring the mass of material. The hydration is continued for another 5 or 10 minutes. The solution is then filtered through an 11-cm. Whatman's no. 4 filter paper, or any other suitable paper, and washed with hot water until nearly free from chlorides. The filtrate, which amounts to 200 or 250 cc. is heated to boiling, and sulfur is precipitated with 10 cc. of a 10 per cent solution of $BaCl_2$, and allowed to stand for 24 hours with occasional stirring. The precipitate is slow in forming and for this reason the standing for two days is sometimes desirable. The precipitate is filtered on a previously weighed Gooch crucible with the use of a substantial mat of long fiber asbestos and moderate suction. The precipitate should be washed five or six times with hot water, dried and the contents ignited in the Gooch crucible at a low temperature. The crucible is cooled in a desiccator and weighed. The percentage of sulfur in the barium sulfate is 13.7343.

The sulfur content of the reagents should be determined, and subtracted from that found in the soil. The blank can be determined either by a direct analysis of the reagents or by determining the sulfur in two different amounts of the same soil. A convenient ratio of one amount to another is 2 to 1, or 3 gm. and 1.5 gm. of soil. Then, twice the amount of sulfur in 1.5 gm. minus the amount obtained from 3 gm. will give the amount of sulfur contained in the reagents. Or,

$$2(a + x) - (2a + x) = x.$$

when x = amount of sulfur in reagents, and a = amount of sulfur in 1.5 gm of soil.

In using ten Parr ignition bombs, which may constitute a set, and three frames for the bombs, one can conduct the explosions nearly as fast as one can make fusions in open iron crucibles, the difference in the time consumed being due to closing the bombs before and opening after the explosion. With one bomb in water for cooling after the explosion, another one on the Bunsen burner, and a third in preparation for heating, one's time will be completely occupied during this part of the process.

<center>EXPERIMENTAL</center>

In offering the above procedure of sulfur determination in soils, it is felt that there is considerable justification for every step in the proposed outline. The soil charge was increased from 2 to 3 grams in order to allow the precipitation of a larger amount of sulfur, which is of considerable advantage in as much as the sulfur content in soils is ordinarily very low.

Granulated magnesium metal, is a very good accelerator of the reaction, and is usually fairly free from sulfur. Some preliminary work showed that about 0.5 gm. of granulated magnesium is the right amount to use with 3 gm. of soil and 10 to 15 gm. of sodium peroxide. A smaller amount of magnesium retards the reaction, making it difficult to notice the explosion. Larger amounts of magnesium, on the other hand, cause the reaction to proceed so violently that bursting of the bomb may result. Ten or twelve grams of sodium per-

oxide were found to be sufficient with an ordinary charge of soil. Larger amounts of peroxide cause an increase in the salt content of the resultant solution, which makes the subsequent precipitation of sulfates difficult.

Amount of hydrochloric acid to use

In taking up the dehydrated mass, 10 or 15 cc. of 1 : 1 HCl is sufficient. When the dehydrated mass is taken up with this small amount of hydrochloric acid, the sulfur may be precipitated without neutralizing the acidity of the resultant solution, as may be judged from the results of an experiment presented in table 1. In this experiment, samples of the same soil were so treated that a difference in the acidity present existed at the time of the precipitation of the sulfur. Table 1 is self-explanatory. The averages of two

TABLE 1

Effect of the degree of acidity of the solution upon the amount of BaSO₄ obtained in sulfur determinations

	TREATMENT OF SOLUTION BEFORE PRECIPITATING SULFUR	AMOUNT BaSO₄ OBTAINED
		gm.
1	10 cc. 1:1 HCl used in taking up material after dehydrating silica......	0.0120
2	15 cc. of 1:1 HCl used in taking up material after dehydrating silica....	0.0114
3	Same as (2) plus 15 cc. 1:1 HCl just before precipitation of sulfur......	0.0107
4	Same as (2) plus 30 cc. 1:1 HCl just before precipitation of sulfur......	0.0098
5	Same as (2) plus 30 cc. concentrated HCl just before precipitation of sulfur........	0.0034
6	Same as (1) plus 2.5 cc. concentrated ammonia to nearly neutralize the acidity of the solution........	0.0115

determinations are given in all the tables. The results show that samples with treatments of 10 and 15 cc. of 1 : 1 HCl, as well as those in which the resultant solution was neutralized, gave practically the same amounts of BaSO₄ in the precipitate, the respective figures being 0.0120, 0.0114, and 0.0115 gm. BaSO₄. With the increase in acidity of solution before the precipitation of the sulfates, the amount of BaSO₄ was proportionally decreased.

It may be noticed in passing that, when 10 or 15 cc. 1 : 1 HCl are added to the dehydrated mass, the effective acidity due to this acid is very materially decreased by evaporation on heating, and also by the buffer action of various salts in solution. The trials show that less than 3 cc. of strong ammonia water is sufficient to neutralize the acid present in the resultant solution in which a dedydrated material was treated with 10 cc. 1 : 1 HCl. A larger amount of added HCl would lose proportionally a large percentage of its effective acidity.

Iron and aluminum should not be removed

The question of whether or not to precipitate iron, aluminum, etc., before precipitating sulfur, deserves special attention since precipitated iron has a large capacity for absorbing the sulfates. A complete washing of sulfates from hydroxide is a very difficult task. The following experiment throws some light on the subject.

Two soils were treated with $CaSO_4$ before fusion with sodium peroxide. After the fusion sulfur was determined in these soils in the presence of iron and aluminum, and also after iron and aluminum were removed by a double precipitation with ammonium hydroxide. The combined filtrates amounting to 400 cc. were reduced to about 200 cc. by evaporation, and the sulfur precipitated as in the samples where iron and aluminum were not removed. The results are presented in table 2. They show that all the added sulfur was ob-

TABLE 2

Effect of iron and aluminum precipitation on sulfur determination and sulfur recovery; amount of $BaSO_4$ obtained from soils treated or untreated with $CaSO_4$, and also from $CaSO_4$ solution

SOIL NUMBER	TREATMENT	PRECIPITATED IN PRESENCE OF IRON AND ALUMINUM		IRON AND ALUMINUM REMOVED BEFORE SULFATES WERE PRECIPITATED	
		As determined in soil	$BaSO_4$ due to sulfur added as $CaSO_4$	As determined in soil	$BaSO_4$ due to sulfur added as $CaSO_4$
		gm.	*gm.*	*gm.*	*gm.*
S3286	Untreated....................	0.0119		0.0068	
S3286	0.05 gm. $CaSO_4$.................	0.0935	0.0816	0.0654	0.0586
5133	Untreated....................	0.0050		0.0025	
5133	0.05 gm. $CaSO_4$.................	0.0859	0.0809	0.0644	0.0619
0.05 gm. of $CaSO_4$ (no soil).................			0.0808		0.0808

tained (after subtracting the amount found in the untreated soil) in samples where iron and aluminum were not removed. On the other hand, when iron and aluminum were removed, there was a considerable amount of sulfur lost in both the treated and untreated soils. It would seem, therefore, that, unless one is very careful to remove all sulfates from the iron and aluminum precipitate, it would be a dangerous procedure to remove iron and aluminum by precipitating them with ammonia. Perhaps other means of precipitating iron and aluminum are less dangerous for a sulfur determination. The removal of iron and aluminum is unnecessary, since iron, aluminum, or mixtures of the two elements have no effect on sulfur determination, when these elements are present in the form of chlorides. The following experiment confirms this view.

Portions of an ammonium sulfate solution, containing 0.05 gm. ammonium sulfate, were treated with a solution of $FeCl_3$, $AlCl_3$, or with a mixture of

the two salts, each portion containing 0.2 gm. of salt. After dilution, the sulfates were precipitated and the sulfur determined. The results are presented in table 3. They show that iron and aluminum present in solution did not reduce to any considerable extent the amount of sulfur obtained as $BaSO_4$.

The results obtained in this experiment, as well as those in the preceeding experiment, show very conclusively that, firstly, the removal of iron and aluminum is unnecessary, and, secondly, it is a dangerous step from the standpoint of accuracy in sulfur determinations.

Barium sulfate could be filtered after 24 hours

The next question studied concerned the method of adding $BaCl_2$ in precipitating the sulfates. Several procedures were tried; precipitating in cold, warm (about 50°F.), or in boiling solutions. The solutions were also boiled and kept on the steam bath for two hours; or, after precipitation in the cold the liquid was kept on the steam bath for 2 hours. In every case, the solutions were afterwards allowed to stand for at least 24 hours but were well stirred

TABLE 3

Effect of iron and aluminum chlorides on sulfur determination from ammonium sulfate solution

TREATMENT OF SOLUTION	AMOUNT OF BaSO₄ OBTAINED
	gm.
0.05 gm. ammonium sulfate alone.	0.0914
0.05 gm. ammonium sulfate + 0.2 gm. FeCl₃.	0.0908
0.05 gm. ammonium sulfate + 0.2 gm. AlCl₃.	0.0909
0.05 gm. ammonium sulfate + 0.2 gm. FeCl₃ + 0.2 gm. AlCl₃.	0.0909
0.2 gm. FeCl₃ + 0.2 gm. AlCl₃ (no ammonium sulfate).	0.0000

several times during the period. The results were practically the same in all cases. The only difference observed was in the physical condition of the precipitates. The samples that were precipitated in the boiling solution, or those heated on a steam bath for two hours, had much coarser particles than those obtained in cold or slightly warm solutions. At least, the settling of the precipitates was more complete and the supernatant liquid was clearer in the former than in the latter cases. Such mechanical differences are of some advantage in filtering either through asbestos or filter paper.

With small amounts present in ordinary soils, the precipitation of sulfur is a very slow process, especially when some silicates are present in solution. There is naturally the question as to how much time is required for a complete precipitation of sulfates, or, in other words, how long one should leave the precipitates stand before filtering. In order to answer this question, the solutions to which $BaCl_2$ was added were allowed to stand for one, two, four and eight days, respectively, before filtering. During the first 24 hours the solutions were stirred several times. The solutions that stood for longer periods were stirred once a day after the first day.

Results from four different soils are presented in table 4. They show that the precipitation is completed during the first 24 hours.

The filtering of barium sulfate may be done on a double thickness of "blue ribbon S and S" German filter paper, which holds the sulfate fairly well, or on some other suitable paper. The filtering through paper is, however, very slow. Besides, it requires considerable heat to burn the paper, and a high temperature tends to decompose barium sulfate. For this reason, Gooch crucibles with a good mat of long fiber asbestos and an application of moderate suction are recommended. It should be noted that asbestos sometimes persists in gradually washing out, i.e., the freshly made Gooch crucible may lose weight on repeated washing and drying. The prepared crucibles should come, of course, to a constant weight before they are used for the filtering of sulfates.

TABLE 4

Time required for complete precipitation of BaSO₄

SOIL NUMBER	NUMBER OF DAYS ALLOWED TO STAND BEFORE FILTERING THE PRECIPITATED BaSO₄			
	1 day	2 days	3 days	8 days
	gm.	*gm.*	*gm.*	*gm.*
3712	0.0070	0.0072	0.0073	0.0076
5133	0.0047	0.0037	0.0048	0.0048
5156	0.0020	0.0018	0.0025	0.0021
S3286	0.0122	0.0117	0.0118	0.0117

CONCLUSION

A method for sulfur determination in soils is presented which, for the past three years, has been successfully used at the Illllinois Experiment Station. It is a modification of the method described by Olson, as developed at the Washington Experiment Station. Some results are presented that justify the adoption of every step in the proposed procedure. Being a very short one, this method is well adapted for investigations where a large number of determinations are made.

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THE ALKALI SOILS IN HUNGARY AND THEIR RECLAMATION[1]

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After a short historical introduction on the reclamation work done in Hungary, dating as far back as the year 1769, the author discusses the different theories on the origin and specific character of alkali soils, and concludes, from his experiences, that for the genesis of alkali soils chiefly three factors are responsible.

These are namely: (*a*) the arid or semiarid climate, (*b*) an imprevious subsoil, (*c*) peculiar hydrological circumstances enabling an intermittent superabundance of moisture in the soil.

He points out, that alkali soils are not simply soils infiltrated by alkali salts. They represent rather a specific soil type of the arid climatic zone, and are the result of a peculiar chemical decomposition of the soil, derived from the effect of alkali salt solutions on the zeolitic and organic compounds of the soil. The displacing of the Ca ion by Na occurs because of the fact that the surface horizons are more or less poor in active calcium, and consequently the colloids of the surface layer percolate downward, forming a more or less impervious accumulation horizon under the alluvial surface horizon.

The washing out of alkali salts does not interfere with the alkali character of the soil. There are in Hungary many alkali soils, which are not harmful with their slight alkali salt-content, but are difficult to till, and unproductive on account of their bad physical properties. By direct experiments the author proved that in displacing the Na ions of the zeolitic-humic compounds by Ca ions, the impervious alkali soils could be changed into permeable soils of good tilth and texture. By infiltrating sodium salts and displacing the Ca ions of a productive neutral soil of good tilth and texture, the permeability and physical properties are made similar to those found in alkali soils, thus showing the artificial formation of an alkali soil.

The author treats of different types of Hungarian alkali soils, called "szik" soils, ranging them in different well defined groups and classes. He describes the territorial distribution of these different varieties, which make up a considerable part of the large plain, called "Alföld," which are mostly unproductive or very poor. He finds by geological, prehistorical, and historical statements,

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[1] A short report on the author's Monograph, laureated by the Hungarian Academy of Sciences, Budapest and the Society of Hungarian Engineers.

that these territories were yearly more or less flooded by water, becoming dry again during the hot and dry summer period, thus causing the alkali salt to come to the surface by capillarity and changing the nature of the soil. But water logging was possible only where the filtration of water through the soil was prevented, either by some impervious clay subsoil, or by some calciferous hardpan, and where the water level in the subsoil was very near to the surface, even during the dry period.

In the early chapters the author deals systematically with the chief physical and chemical properties of the various "szik" soils. Numerous analytical and experimental data are given.

Summarizing these results he finds that the porosity of the heavy "szik" soils is very low, the water-holding capacity, on the other hand, is very high. The result is, that when saturated with water, the soil has no air capacity. This is one principal reason for its unproductiveness. The mechanical composition, though very different in the several types, is mostly very fine, the fine silt and clay making up the main part of the soil particles. Only a small part of it is of sandy character, but also in this case some kind of colloidal lime carbonate cements the coarse and fine sand. Thus the sandy soil becomes nearly impermeable to water, especially to a sodium carbonate solution, which is very abundant in this particular type of "szik" soil. As a whole the loamy and clay alkali soils are impermeable and their capillary power very deficient. Consequently the water movement in the soil is practically prevented. This is another reason for the unproductivity of these soils. As regards the plasticity and hardness of the soil, the heavy clay "szik" soils may be arranged in the highest class of Atterberg's classification. This explains the difficulty of tilling this type of soil. The high shrinking power of these soils causes the formation of very deep cracks or numerous fissures into which the muddy superficial floodings percolate, giving to the profile a peculiar veined appearance of irregular prismatic or columnar shape. The wilting coefficient is very high, accounting for the rapid extermination of any vegetation during the dry season.

As regards the chemical character of the different "szik" soils we have to arrange them in two main groups. In one group the aluminum silicates are superabundant, in the other, the lime carbonates. The latter are mainly black alkali soils, like the alkali soils in Fresno, Cal. The whole alkali territory lying between the Danube and Tisza belongs to this type of "szik" soil. On the other hand, the heavy clay "szik" soils along the Tisza river and its tributary streams are often lacking in carbonates and are mainly infiltrated by either sulfates like the alkali soil type of Billings, Montana, or sulfates partly intermixed with carbonate and chloride of soda, like the Salt Lake type of alkali in Utah.

The author also describes different methods of reclamation, dividing them into four groups according to their main characteristics, namely:

1. Physical reclamation methods
2. Methods of removing alkali
3. Chemical methods of reclamation
4. Biological methods of reclamation

The irrigation problem in Hungary before the war depended on the storing of water in the peripherical highland territories. As these water storing highlands have been cut off by territorial changes, physical and chemical methods are of most importance. These are methods of dry-farming, and consist of liming, manuring, tilling the soil, covering with a yellow marl, and draining surface-water to prevent the formation of earth crusts. In this way, a good wheat crop is harvested, but only a part of the "szik" soil is reclaimable in that way. By storing the rainfall in the spring, the alkali is washed deep enough in the subsoil so as to get a fair hay crop and good pasture, which is very important for cattle breeding in this dry country. With the limited irrigation water there is a successful system of surface irrigation requiring less irrigation water than the flooding system used in America. It is true, that the removal of alkali is slower and not so perfect as by washing through the soil. But the latter seems very often an insolvable problem, if we consider the impermeability of most of this alkali land. The establishment of fisheries on alkali land also was very successful and lucrative, considering the limitations of the fishing industry of the country. The reclamation work is now stopped chiefly because of lack of capital.

SOIL ACIDITY IN RELATION TO SOIL TYPE GROUPS, IN NACOGDOCHES COUNTY, TEXAS

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With the recent development of numerous field tests for the estimation of acidity, the relation of soil acidity to soil types is receiving a great deal of attention, particularly by those associated with soil classification work.

In order to obtain as exact information as possible regarding the prevailing soil reaction of the various types encountered in the field, the writer, in the course of the soil survey of Nacogdoches County, Texas (winter assignment 1923–1924) made over 200 acidity tests using neutral litmus paper[1] and the Soil-tex solution.

Nacogdoches County, in the central part of East Texas, lies entirely within the Interior Gulf Coastal Plain. The topography is rolling to hilly, the county as a whole being well dissected and well drained by numerous streams. The mean annual rainfall is 47 inches; the growing season about 240 days.

The soils of the county are derived from the unconsolidated sands, sandy clays, and clays of marine origin which constitute the underlying material of the Coastal Plain, extending from East Texas eastward across the Gulf states and well up along the Atlantic seaboard. The most extensive soils found in the county belong to the well-known Norfolk, Orangeburg, Ruston, Kirvin, and Susquehanna series. These are all upland types, having good regional drainage.

Concerning regional characters, these soils are low in organic matter, low in lime, and low in available plant-food. Under virgin conditions, these soils have 3 well-marked horizons, or soil layers, the lowest resting upon parent material. The first horizon consists of 2 or 3 inches of dark gray mineral soil, containing slight to moderate amounts of organic matter. The second horizon is well-oxidized and well-leached mineral soil, light colored, usually pale yellow to yellowish- or reddish-gray. The third horizon is the highly pigmented yellow, yellowish-red or red sand, sandy clay, or clay, characteristic of the region. The parent material immediately underlying these types is noncalcareous.

Inasmuch as the reactions of certain closely related types proved very similar, for the sake of brevity convenient groupings are made as follows:

1. Sandhills (Norfolk and Ruston fine sand).
2. Fine sands with sandy clay subsoils (Norfolk, Ruston and Orangeburg fine sandy loams).

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3. Fine sands with clay subsoils (Kirvin fine sandy loam).
4. Fine sands with mottled, plastic clay subsoils (Susquehanna fine sandy loam).
5. Clay loam with mottled, plastic clay subsoils (Susquehanna clay loam).

Acidity tests were made of virgin soils only, and according to natural soil horizons. Particular care was taken to be certain the samples were representative. The mean acidity for each type group is shown graphically in figure 1.

It may be noted, at the outset, that the reactions of the first horizons are quite similar for the various soil groups represented. This condition appar-
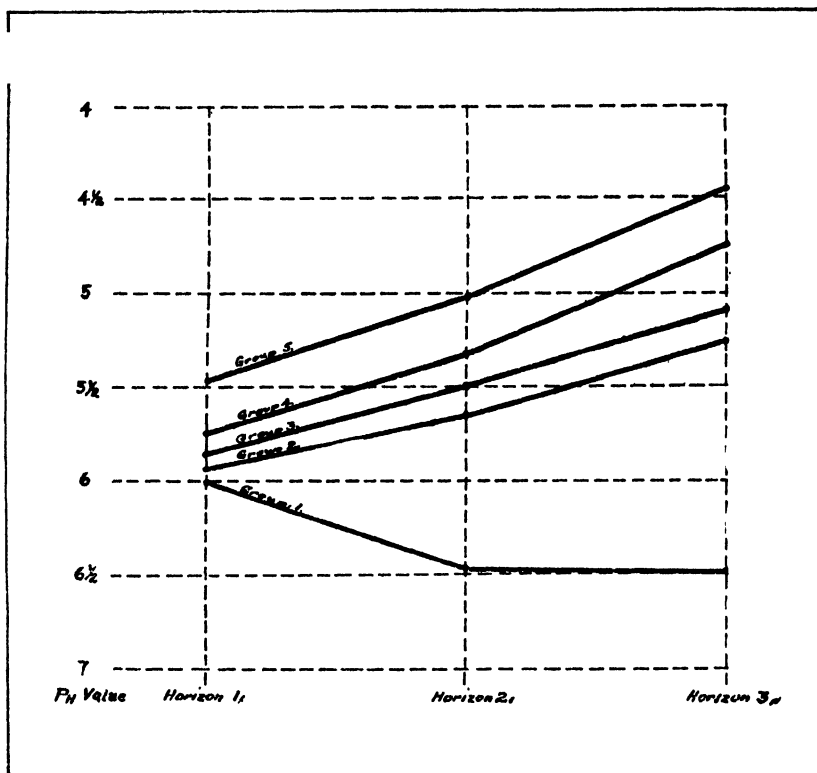
FIG. 1. MEAN ACIDITY FOR SOIL TYPE GROUPS

ently reflects the common character, namely, the surface organic layer. Below this horizon, the several groups vary, one from the other, in textural and structural character, and as regards aeration and internal drainage.[2] Correspondingly, the soil-reaction curves for the separate groups diverge, as shown, for increasing depths below the surface. Increasing acidity is invariably asso-

[2] For detailed descriptions of the soil types concerned, the reader is referred to Marbut, C. F., Bennett, H. H., Lapham, J. E., and Lapham, M. H., "Soils of the United States," U. S. Dept. Agr. Bur. Soils Bul. 96.

ciated with finer textures, poorer aeration, and poorer internal drainage conditions. Thus, the deep fine sands of the Sandhill group, which are deep, open-structured, well aerated and well drained, and without textural change in the 3-foot section, show the least acidity. The second group, consisting of 12 inches of fine sand overlying a subsoil of well oxidized, well drained, friable sandy clay, shows increasing acidity, most marked in the third horizon. Group 3, represented by a type consisting of 12 inches of fine sand, over a subsoil of well oxidized, well drained clay, shows a slightly higher acidity. Group 4, for which is used a type of fine sand 12 inches deep, overlying stiff, plastic clay, passing at 18 to 24 inches into a mottled plastic clay, with poor aeration and poor internal drainage, indicates a still higher acidity, becoming abruptly intense in the mottled subsoil. Group 5, represented by a clay loam, underlaid at shallow depths by a plastic clay, passing into a heavy, mottled, plastic clay deeper subsoil, with poor aeration and very poor internal drainage, shows the greatest acidity, the maximum of which is again found in the mottled subsoil.

Causes of variations in reaction within the soil type were found to be almost entirely traceable to discernible physical variations within the type. For example, areas occupying more gently sloping topographic position than usual were found to have a slightly higher acidity than normal for the type, probably due to increased organic content, finer textures, poorer internal and regional drainage conditions, or a combination of the above.

It further appears from this study, that the acidity relationship, as regards drainage conditions, depends more upon the internal drainage than upon the regional drainage. In support of this,—the highest acidity found in the county, (including many tests made of deoxidized lowland and swamp soils) was found existing in the Susquehanna clay loam, group 5, the tests being made at the tops of abrupt knolls in steeply rolling country.

Finally, it is apparent that, under climatic conditions tending to produce soils well leached of lime carbonates, it is entirely possible to estimate the mean acidity content of well developed, well weathered types, and to show fairly consistent differences between the acidity content of diverse types of this character.

THE CHEMICO-PHYSICAL INFLUENCES OF QUICK LIME AND CALCIUM CARBONATES ON MINERAL SOILS[1]

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The investigations of the last decade have brought us the fundamental knowledge of the effects of quick lime and calcium carbonate on the soil.

In carrying out the work reported in this paper, it was deemed necessary first of all to make a preliminary study of the chemical and physical phenomena of pure soil constituents. The native soils are of a complex composition, the constituents of which can hardly be isolated. Therefore its problems cannot be studied adequately unless the behavior of the separate soil constituents has been demonstrated by typical examples. Fine granulated quartz was used in the experiment as a representative of a widespread soil constituent, chemically almost inactive. Permutites were further used which, in comparison with the most active soil silicates, show only such differences as might be expected for gels of different ages and prepared by different methods. The greatest part of the experimental work was done by Hermann Sallinger, Josef Danzl and Hugo Junk. The summarized details will be published later.

I. ADSORPTION BY QUARTZ

Purified quartz with particles of a 0.002-mm. diameter was used in the following experiments. The effect of solutions on the quartz suspensions was studied by adding 50 cc. of solution to 50 cc. of suspension (containing 10 to 20 gm. of quartz), so that the total volume in each experiment was 100 cc. The quantity adsorbed changed considerably with the concentration. The figures mentioned for the adsorbed quantities concern solutions of 0.00224 normality. The values can be reproduced under identical experimental conditions. They are therefore transmittable.

1. Swelling values

The swelling value of a material is indicated by the concentration of a solution at which a quick settling of the suspended particles takes place. The knowledge of the swelling values is of importance in soil studies because it gives an idea of the effect of the material on the flocculation of the soil particles

and therefore of the formation and preservation of soil crumbling. This relation is to be considered in this way—the soil settles if the concentration of the solution of a compound is greater than the swelling value. However, well crumbled soils may be maintained at concentrations lower than the swelling value. The whole behavior of the soils indicates that there is a relation between the swelling values and the natural soil structure. Based on the swelling values of quartz the swelling values of the most important hydroxides of the bivalent metals [$Ca(OH)_2$, $Ba(OH)_2$, $Si(OH)_2$] are at a concentration of $0.00035N$. For univalent metals (KOH, NaOH) the concentration is $0.1N$. The effectiveness of the bivalent metals therefore is 300 times as great as for the univalent metals. Expressed in terms of weights, the amounts of the various substances necessary to flocculate a quartz suspension in 1 liter of solution are as follows:

	grams		grams
Calcium hydroxide	0.013	Potassium carbonate	3.5
Potassium hydroxide	5.6	Sodium carbonate	3.2
Sodium hydroxide	4.0	Magnesium carbonate	0.2
		Acid calcium carbonate	0.25

Thus the effectiveness of calcium hydroxide expressed in terms of weights is 430 times as great as that of potassium hydroxide, 300 times as great as that of sodium hydroxide, 266 times as great as that of potassium carbonate, and 245 times as great as that of sodium carbonate. The solubility of calcium carbonate is too little to measure the swelling value directly. The swelling value of acid calcium carbonate ($0.009N$) is about the same as that for calcium chloride ($0.01N$). In general the swelling values of the salts of many metals are about the same, for example:

Potassium carbonate	$0.05N$
Potassium chloride	$0.045N$
Sodium carbonate	$0.06N$
Sodium chloride	$0.055N$

The great differences which occur, if expressed in terms of weights, explain the different effects of the strongly active bivalent metals (Ca, Mg) against weakly acting univalent metals (K, Na). The detrimental effects of sodium carbonate on the soil are thus made clear.

2. Adsorptions

Quartz adsorbs strongly alkaline compounds. As far as soil problems are concerned these compounds are mainly hydroxides and carbonates. On the other hand, neutral salts and acids are taken up only in traces. To give an idea of the phenomena involved it will be satisfactory to note the quantities taken up by 1 kgm. of quartz (diameter 0.002 mm.) and also calculate it for an area of 1 hectare at the depth of 20 cm. (specific gravity 1.5). The quantities

adsorbed by quartz from 0.00224N solutions in grams and Doppelzentner[a] are as follows:

	1 KGM.	1 HECTARE
	gram	*ds.*
Calcium hydroxide......................................	1.07	32
Potassium hydroxide...................................	0.63	19
Sodium hydroxide......................................	0.44	13
Magnesium carbonate.................................	0.71	21
Potassium carbonate..................................	0.42	13
Sodium carbonate.....................................	0.27	8
Ammonia nitrogen.....................................	0.07	2*

* Adsorption from ammonia; the ammonium hydroxide on account of its low ionic concentration is adsorbed only weakly from solution; ammonia (NH_3), if any, is taken up from solution only in minute quantities.

The variation in adsorption of hydroxides which could be repeated by various soil silicates, indirectly becomes of great moment in the case of liming with quick lime. Most of the contradictions with quick lime experiments, which could not be explained till now, may in all probability be traced to the phenomena mentioned.

II. EXCHANGE OF BASES

The processes of the exchange of bases in the soil have been studied in a constantly increasing measure for the last hundred years. In our experiments, rather homogeneous permutite was used, which was obtained from the Permutite Company (Permutit-Aktien Gesellschaft). It was produced by the wet process and is a sodium permutite with a low calcium content. The exchange of the bases of the permutite is subject to the following rules (in agreement with the processes in the soil):

The base exchange takes place in equivalent quantities. The taking up and giving off of the metals depends on the relation of the ions in the solution and differs for the various metals. Therefore, the metals combined in a permutite will exchange completely or incompletely for those present in the solution. The more easily a metal is taken up by a permutite and the more completely it is exchanged for combined metals there present, the more difficultly and incompletely will it be displaced from the permutite by other metals. If the metals investigated were arranged according to the quantities in which they were absorbed by the permutite they would form a successive series which, with a few transpositions, corresponds to the lyophilic series of colloid chemistry.

[a] A Doppelzentner = 100 kgm.

$$Mg < Li < Ca < Na < Ba < NH_4 < K < \ldots . H$$

Very probably hydrogen is the last link of this chain.   The place of the metals in this series seems to be closely connected with the hydration of their ions.

Besides the exchange of bases between the ions of the solution and the silicate, other chemical or physical phenomena frequently enter which may influence strongly the course of the transformations.

The following rules may be established:

1. Neutral salts exchange in equivalent quantities (acid carbonates behave like neutral salts).

2. Hydroxides and alkaline compounds exchange in equivalent quantities, but at the same time there occurs the combination of hydroxides which can be traced back either to adsorption influences or to the formation of basic salts. In higher concentrations of hydroxyl ions, a chemical decomposition of the permutite silicates will result.

The action of soluble hydroxides and alkaline solutions on the silicates capable of exchange calls forth a change—which may be considered either as exchange of bases, adsorption, or decomposition of silicates, depending on the concentration of the solutions and the properties of the compounds present.

In the permutite experiments, hydroxides exchanged in equivalent ratio; at the same time approximately the same quantity of hydroxide was combined either by adsorption or by the formation of basic salts.   It may be accepted as a rule, that from the hydroxide solution of a silicate, equal quantities of hydroxide are exchanged and combined.   This, however, is true only for the silicates capable of exchange.   Quartz and other soil constituents become active by their own adsorption.

The decomposing action of the hydroxides on permutites was detectable in the experiments only after longer periods (a few days).   The course of these processes has not yet been studied.

III. ACIDS AND ACID-REACTING SOLUTIONS

Strongly active acids, namely solutions with a considerable hydrogen-ion concentration, bring about the decomposition of the silicates capable of exchange.   It seems that partial decomposition of the silicates takes place in solution even at a low hydrogen-ion concentration.   This is indicated by the formation of small quantities of aluminum and silicic acids in the solution; for the bulk of the silicate molecule an exchange of its cations with hydrogen is to be accepted, which means the formation of complex aluminum-silicic acids (permutite acids).   This is corroborated by the fact that it is easy to restore permutites to their original effectiveness and constitution (regeneration of the permutite), by means of alkaline compounds if the loss of bases was the result of treating them with low acid concentrations.   *The hydrogen of the permutite, on the other hand, is exchanged only very incompletely by cations of neutral salts.* This is a very important fact in soil fertility, since the formation of mineral acid soils is based on it.   The occurrence of such formation is much more

frequent than is generally known and deserves more attention, especially in so far as it is related to the chemical transformations in the soil.

If permutites free from their basic cations (corresponding to the silicates of mineral acid soils) are treated with neutral salt solutions, an exchange of hydrogen for cations of the neutral salts will result first to a rather large extent; upon addition of more neutral salt solution, the exchange decreases quickly and soon it will be so small that it can be practically neglected. This solution shows an acid reaction corresponding to the titration-acidity of an equivalent amount of aluminum present in solution. The exchange will not stop with another addition of neutral salt solution, but it will be reduced to traces. This is also true in the case of potassium chloride solution (Daikuhara method). In general, all permutites possessing a cation hard to replace behave identically toward solutions with little of active cations (see series of cations). When a permutite free from its bases was treated 26 times with potassium chloride solution, only 2 per cent of the hydrogen was given off, which corresponds to the amount present in the permutite according to other analytical figures. This means that the methods formerly used for the determination of the acid content of a mineral acid soil furnish figures lower than the real content.

The exchange of the basic hydrogen for hydroxides and alkaline salts is, on the other hand, complete. The calculated hydrogen content and the quantity of ammonia taken up by the permutite was in agreement when the permutite was treated with ammonia, as mentioned above. It may be pointed out here that a treatment with ammonia solution is promising for the determination of acid in purely mineral soils. Approximately the right values may be obtained, as only very slight amounts are adsorbed from the ammonia solution. On the other hand, the strong adsorption which takes place from solutions of bivalent hydroxides—lime and barium hydroxide (Veitch method), will give figures double those indicating the true acid content of the soil.

Free carbon dioxide

The decomposition of the silicates depends on the concentration of free hydrogen-ions in the acids. Besides organic acids, carbon dioxide is active in the soil. The carbon dioxide[3] of the soil solution is practically completely dissociated into $H + HCO_3$ ions. The concentration of the carbon-dioxide ions is small and increases only slightly with increasing pressure of the carbon dioxide and its solubility in water which depends upon it. For soils and rocks the influence of the carbon dioxide may be considered as constant without introducing an appreciable error, even when the carbon-dioxide pressure is high (50 atmospheres and over).[4]

[3] Carbon dioxide (CO_2) very often called "carbonic acid" is a water-soluble gas, but only a small part of the dissolved CO_2 is combined with water under formation of carbonic acid (H_2CO_3).

[4] The solubility of carbonates under the formation of soluble acid salts (calcium, magnesium, or ferrous oxide) is influenced strongly with an increase in carbon-dioxide pressure.

The action of carbonic acid on permutite was investigated. It is very probable that the phenomena observed are also true for other silicates. The permutites are to be considered as the most unstable type of silicates. The attack by carbon dioxide is strong in the beginning but gradually decreases and goes on very slowly afterward. Water saturated with carbon dioxide at atmospheric pressure, lessened the normality of sodium permutite from 0.4526 to:

$0.2104N$ if 1 liter was dripped on
$0.1933N$ if 2 liters were dripped on
$0.1940N$ if 3 liters were dripped on
$0.0927N$ if 10 liters were dripped on

The decomposing action of the carbonated water was slight. It was indicated by the formation of small quantities of aluminum compounds and silicic acids in the solution. In the majority of permutites, sodium was exchanged for hydrogen, thus forming "permutitic acid."

Buffer actions

The investigations were concerned with mineral soils and dealt only with buffer actions in a classic sense, i.e., with the effects on the ion concentration in the solution and on the solubility of the compounds formed.

The acid carbonates of the soil solution exert strong buffer actions, inasmuch as the hydrogen-ion concentration of the free carbon dioxide is strongly forced back. The extent to which such an action may go is demonstrated by the fact that the "disbasing" of a permutite by water saturated with acid calcium carbonate (at 1 atm. CO_2 pressure) was forced back to 1/500 of the effects of salt-free carbonated water.

The buffer action of the acid carbonates in the soil is very evident. The upper layer of forest soils reacts (according to Gustav Krauss) almost always acid; this acid reaction diminishes quickly, however, in the deeper soil layers. On slight depth (5 to 10 cm.) the reaction is already neutral in most cases, while it will be faintly alkaline on greater depths. In regard to the relation of the rôle played by the carbonates in the soil, it is important to estimate besides the saturation of the free acid also the buffer action of the acid carbonates. This prevents largely the decomposition of the exchanging soil silicates and makes the exchange of bases safer.

Another process which influences the transformation of quick lime is the effect of alkalies present in the soil solution on the solubility of calcium hydroxide. Sodium hydroxide solution of 0.1 normality suffices to precipitate practically all the dissolved calcium hydroxide. Such high concentrations do not occur in soils, but much lower concentrations give evidence of this phenomenon, which accelerates the undesired effects of the alkali hydroxides.

Degree of saturation ("Sättigungsgrad") of soils

The influence on soil conditions exerted by the combining of metals has long since attracted attention. There is considerable difference between the effects of uni- and bi-valent metals. Calcium, magnesium, perhaps also aluminum and iron as bivalent metals; and the alkalies, chiefly sodium, as univalent metals; and further, hydrogen, are of importance for the soil. The first group accelerates the properties of settling and crumbling, and lowers the adhering qualities of the separate soil particles. The second group increases the coherence of particles, the soil gets more or less slimy, and the crumbling is less. A generally adopted definition for the "Sättigungsgrad" of a soil has not yet been established. Among the earlier investigators who studied the problem of soil saturation, Hissink (1) defines "Sättigung" or "Sättigungsgrad" of a soil as the difference between the adsorbable bases and those combined in the soil. Sokolovski (2) regards essentially only calcium, and means by "Sättigungsgrad" more or less saturation of the soil with calcium, thus considering his practical experience that the soil properties depend largely on the quantities of lime combined with the soil.

The unsaturated condition of mineral soils is evidently the result of freeing the soils from bases by acids, mainly carbonic acid. Therefore, it coincides predominantly with the rate of soil acidity. For soils rich in humus, the inadequately studied humic-acid compounds are to be taken into consideration. As yet no reliable method for the determination of the "Sättigungsgrad" of the soil has been found. On the basis of base exchange, pure mineral soils treated with ammonia, or in general with calcium-or barium-hydroxide solutions, give figures which serve as a guide for the determination of the saturation of the soil. On account of the high adsorption of bivalent hydroxides, the figures obtained should be halved. The working out of a reliable method for the determination of the saturation rate is a necessity for the study of the theoretical and still more the practical soil problems.

Adsorbability of exchangeable bases for plants

It is known that plants are able to absorb basic plant nutrients. A number of sand-culture experiments show that if the proper salts are present in the solution, the exchange of bases satisfies the nutritive needs of the plants. It is doubtful whether the plant roots are able to absorb directly basic nutrients from permutite bases without intervention of the exchanging salt solutions. Attempts to grow plants with permutites as the only source of available bases were not successful. Soil silicates incapable of base exchange but which could be decomposed by hydrochloric acid gave quantities of plant nutrients not even worth mentioning. It seems that the plant takes its nutrients only from compounds present in solution or from those which are made soluble by the exchange of bases (see Nostitz).

Quick lime and limestone fertilising

The experimental results mentioned enable us to get an idea of the transformations which take place in the soil after an application of quick lime. These transformations are more complicated than they were believed to be until recently. They depend not only on the physical, but also largely on the chemical composition of the soil.

The flocculation effect of quick lime shows up when the swelling value in the solution has been reached. Compared with the swelling value of quartz, which is 0.013 gm. per liter, and assuming that the water content of the soil is 20 to 30 per cent by volume, this being the average water content for heavier soils, the quantity of calcium hydroxide necessary for the settling of 1 liter of soil (sp. gr. 1.5) amounts to from 0.0025 to 0.004 gm. This corresponds to an application of 5 to 10 kgm. of quick lime per hectare. This quantity, however, should be available in the soil solution in order to produce the desired physical action; it will correspond to approximately $pH^5 = 10.5$. It is known that when a soil has been flocculated once it can maintain the condition rather well, provided it is not disturbed by action of mechanical agents. Therefore, the soil crumbling will also be maintained when the hydroxide has been transformed by carbon dioxide to carbonate. It should be noted that the carbonate itself possesses properties which favor the formation of soil crumbles and it may be assumed that a certain quantity of dissolved calcium hydroxide has to be present in the soil in order to produce the desired physical action. For this reason an application of quick lime should be given at such a rate that a moderate excess remains in the soil solution. On account of the fact that an alkaline soil reaction is of disadvantage to the majority of crops, quick lime should be applied to the soil sufficiently early that the greatest part of the lime will have been precipitated from the soil solution as carbonate at the beginning of the growing process.

Adsorption and base exchange

Considerable quantities of calcium hydroxide are combined in the soil by adsorption and exchange of bases. The soil solution loses its bases by adsorption and becomes more or less inactive for the plants. The base is taken up from the soil solution and the alkaline reaction disappears or is considerably lessened without making the calcium inaccessible to the plant roots.

In relation to the exchange of bases it has to be considered whether a soil is more or less freed from bases, i.e., has an acid reaction. The result is an exchange between calcium and the basic hydrogen of the soil silicates and the formation of calcium silicates and water. This process improves the soil, the exchangeable silicates becoming more active in their chemical and physical properties through the replacement of the slowly acting hydrogen by the easily

[5] Translation doubtful. Interpreted "pH" without consultation with author.

transformable calcium. The exchange of bases is facilitated so that a mineral acid soil may be improved chemically; largely by an application of quick lime. On soils which are strongly reduced in bases, a quick-lime dressing is profitable. If, however, the soil is rich in exchangeable potassium- and sodium-containing silicates, the results may be entirely different. Under these considerations calcium will replace potassium and sodium, which in their turn go into solution as potassium and sodium hydroxide. It is a well known fact that alkali hydroxides are harmful to plant growth if present in very small concentrations.

The alkali hydroxides are much less freely adsorbed by the soil, which is another reason why they are more active than an equivalent quantity of calcium hydroxide.

Compared with the quartz experiments the following computations may be deduced:

A weighed quantity of soil (1 kgm.) with the adsorbability of quartz was treated with solutions of 0.00224N, and it adsorbed:

$$\begin{array}{lll}
\text{Calcium hydroxide} & 1.07 \text{ gm.} = 100 \text{ parts} & \\
\text{Potassium hydroxide} & 0.63 \text{ gm.} = 59 \text{ parts} & (1) \\
\text{Sodium hydroxide} & 0.44 \text{ gm.} = 41 \text{ parts} &
\end{array}$$

The exchange of bases between the solution and the soil silicates proceeds, however, in gram-equivalents, namely $\dfrac{Ca(OH)_2}{2} = 37$; KOH $= 56$; NaOH $= 40$. For each 100 parts of calcium hydroxide adsorbed by the silicates, the following go into solution:

$$\begin{array}{lll}
\text{Potassium hydroxide} & = 151 \text{ parts} & \\
\text{Sodium hydroxide} & = 108 \text{ parts} & (2)
\end{array}$$

The soil thus adsorbs:

$$\begin{array}{lll}
\text{Calcium hydroxide} & = \text{Difference (1) against (2)} & - \\
\text{Potassium hydroxide} & = \text{Difference (1) against (2)} & -92 \\
\text{Sodium hydroxide} & = \text{Difference (1) against (2)} & -67
\end{array}$$

In order to demonstrate this influence we might assume that when a soil with an adsorptive power equal to 100 parts of lime is treated with equivalent quantities of $Ca(OH)_2$, KOH and NaOH no lime will remain in the soil solution, but both potassium and sodium will be present in proportions of 60 and 67 per cent respectively. The alkalinity of the soil increases thus very much and is kept high for a long time, as the alkalies will not be precipitated by CO_2 as the lime is. Why the plants are injured when quick lime is applied to fertile soils, or rather to sand cultures is therefore easily accounted for. It is also clear why quick lime might cause severe injury to the crops if potassium fertilizers have preceded. The injurious factor in those cases is not the lime' but the alkali hydroxides formed.

These facts lead to the rule, that quick lime should be applied at such a rate that the soil is able to adsorb the lime as well as the alkali hydroxides formed.

In order to use quick lime rationally one should be acquainted with the soil, its saturation rate and exchange of bases. It remains for the agricultural chemist to establish simple, practical and reliable methods for the determination of these magnitudes.

The decomposing influences of quick lime and alkali hydroxides on the silicates, as also the transformation of the adsorbed lime, have not yet been studied. That such processes do occur is indicated by the fact t' ·t the quantity of adsorbed lime increases considerably after hours and da s. Nor has the behavior of mixtures of calcium and magnesium oxide and their l drates' (Graukalk) been studied. Not until these problems have been solved can one tell which is more efficient: large quantities of lime at long intervals, or small amounts with short periods between applications.

It is obvious that quick lime as a fertilizer has a very great influence on the soil; its effect is stronger than that of any other fertilizer. If the quick lime is applied to improve the soil structure, it should not be applied at a much higher rate than the soil can adsorb. Soils which are freed from bases are neutralized. Injury to the crops by the formation of alkali hydroxides may result after heavy quick lime dressing on soils of a good chemical composition. In both cases it is appropriate to apply a smaller amount than is indicated by computation figures. In any event the application should not be so much that the soil would not be able to adsorb the alkali hydroxides formed. Quick lime and potassium salts, especially kainit, should not be applied simultaneously, but with a proper period between. It is efficient to apply lime first and then the potassium fertilizer—for instance, lime in the fall and potassium salts the next spring.

IV. LIMING WITH CALCIUM CARBONATE (MARLING)

Calcium carbonate is a very insoluble salt, one liter of CO_2 free water noncontaining 13 mgm. in saturated solution. On account of its low solubility its effectiveness has been ascribed exclusively to its easy transformability into the more soluble acid carbonate under the influence of the CO_2 to the surrounding air. The author thinks it a right presumption for the majority of the German soils, but the slight solubility of the carbonate itself can, under certain conditions, contribute to marked transformations, where acid-reacting soils freed from bases are involved.

Up to the present time the tendency has been to consider the difficultly soluble compounds quite apart from the more soluble substances, their chemical transformations having been regarded as "heterogeneous" reactions. It was assumed that compounds present in solution were acting on the insoluble solid phase. Only in more recent years did we succeed in showing that these processes of "homogeneous systems" proceed in relation to the solubilities of their reacting substances. The difficultly soluble substances go into solution again and again, so that considerable quantities may be transformed during a long period (3).

The occurrence of such transformations in soils have been suggested repeatedly. Their presence can also be shown for calcium carbonate.

If limestone is supplied to acid-reacting soils freed of bases, or to soils showing adsorbability, it will in part be dissolved in the soil solution, but it will be

precipitated out again whenever the solution comes in contact with soil parti-
cles which show an affinity for calcium carbonate. There is a continuous
exchange of $CaCO_3$ between the soil solution and the soil particles. Solution
and precipitation will continue until an equilibrium is reached. If solution
and precipitation take place in separate places, their exchange in the solution
will be established by salt-diffusion. In this way the exchange of $CaCO_3$
in the soil can go very far, notwithstanding its slight solubility, if only a
relatively long time is available. The effectiveness of these processes cannot
be expressed in figures, as they differ for every soil in nature and speed of
reaction. It will be clear that the fineness of the limestone particles is of great
importance. If equal amounts in weight of fine and coarse granulated lime-
stone are applied to a soil, the space distance between the particles diminishes
rapidly. The free distance between two particles is directly proportional to
the diameter of the particles, assuming their percentage in the soil is the same.
(This was calculated for watery suspensions of quartz, but in the same sense it
is true for soil mixtures.)

It is generally stated that the smaller the particles of a substance the faster
it dissolves. This statement is true only to a certain extent. The increase
in solubility with decreasing size of the particle, as found theoretically, reaches
for the size of soil particles values which hardly can be measured. On the other
hand the speed at which the concentration of saturation is reached increases
with the area of the soil particles, thus increasing strongly with decreasing size
of the particles. The effectiveness of difficulty soluble fertilizers (lime and
Thomas slag) depends, therefore, greatly on the size of their particles. It is
clear that little effect may be expected, if the size of the particles corresponds
to fine or medium-sized sand granules. Separate lime particles in the soil
are effective only over a small distance (see appendix).

Through liming, lasting effects were obtained in the neutralization of acid
soils, especially mineral acid soils, although its action was slow. The soil
silicates which lost their bases by exchange, regained their activity, while the
soil structure was improved at the same time. The neutralization of the soil
acids is established by the transformation of calcium carbonate to acid calcium
carbonate. The crumbling effect is not so great, as acid carbonates behave like
neutral salts, while the concentration of most soil solutions does not reach the
swelling value of the salt. On the other hand, extensive physical, perhaps
chemical, influences are caused by the formation of $CaCO_3$ from $Ca(HCO_3)_2$.
The equilibrium is established every time between the soil solution and the
carbonates present in the soil. This equilibrium depends on the CO_2 content
of the surrounding air. The CO_2 content of the soil air increases regularly
with the depth. This increase causes a transformation of $CaCO_3$ to $Ca(HCO_3)_2$.
which dissolves. A decreasing CO_2 content will cause the precipitation of
$CaCO_3$. The latter will take place in dry periods and in arid regions when the
soil water is raised and the soil solution, rich in acid calcium carbonate, rises to

the surface. Precipitation of $CaCO_3$ also takes place in soil layers where through greater diffusion large amounts of CO_2 are given off to the free atmosphere. This process appears everywhere as soon as the rising water movements take place in humid regions during dry periods. The result is the formation in arid regions of soil layers rich in lime. Very probably the calcium carbonate is precipitated in a colloidal form and crystalizes out later. The calcium carbonate is very finely divided during the intermediate state and can hardly be distinguished from a solution. In this form it can be absorbed to a great extent by all soil particles and thus it will possess a great crumbling effect. There are great differences in the use of quick lime and marl. The practical farmer considers their influence on the soil as identical, marl only being slower and milder in its action. This however will be the case only when the quick lime has been transformed into the carbonate by CO_2. As long as the quick lime is present as such, its physico-chemical influence is quite different from that of the calcium carbonate; it affects the soil equilibria to a very large extent.

Our studies are concerned only with the mineral soil constituents, but approximately the same results may be found with humic soil constituents, for instance, the influence of the acidity of humic substances upon soil organisms. The influence exerted by the quick lime on the inorganic and organic colloidal soil constituents will probably be of a similar kind, although it is not impossible that important differences may be found after a more careful knowledge has been obtained on this subject. It seems that certain humus substances which occur in old humus deposits, or in humus soils, have an unfavorable effect on plant growth when quick lime or even marl is applied. There are experiments on record where damage was done to the plants by an application of lime on old pastures or on soils bearing the first crop.

It should always be borne in mind that lime and marl are primarily soil improvers. As a plant nutrient they are of much less importance. The lime application should therefore be in agreement with the conditions of the soil. These conditions should be known as accurately as possible. When the necessary fundamentals of this knowledge have been established, the efficiency of the use of lime will be one of the most important factors for the improvement of the soil and of agriculture in general.

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APPENDIX

Size of particles in relation to fertilizing influences. The relations occurring in quartz suspensions served as a basis for the deduction of the spatial distribution of quantities of soil equal in weight but consisting of particles of different size.

The number of quartz particles (radius $= r\mu$) in m gm. of quartz (s.g. $= 2.65$) $=$

$$= \frac{10^{12} \cdot m}{\frac{4}{3} r^3 \pi \cdot 2.65}$$

Assuming that the particles are equally distributed in V cc. of water, the volume of the suspension will be

$$10^{12} \left[V + \frac{m}{2.65} \right] \mu^3$$

This is the volume of a cube whose edge is

$$L = 10^4 \sqrt[3]{V + \frac{m}{2.65}}\, \mu$$

L corresponds to $N = 10^4 \sqrt[3]{\dfrac{m}{4/3\, r^3 \pi \cdot 2.65}}$ particles.

For each quartz-sphere is thus available a length

$$l = \frac{L}{N}$$

$$l = \sqrt[3]{\frac{\left(V + \dfrac{m}{2.65}\right) \cdot 4\, r^3 \pi \cdot 2.65}{3m}}\, \mu = 2.23075\, r \sqrt[3]{\frac{V}{m} + 0.37735}\, \mu$$

The smallest free distance between two quartz particles is therefore

$$a = l - 2r = 2r \left[1.115 \sqrt[3]{\frac{V}{m} + 0.377} - 1 \right] \mu$$

Thus it is shown that the free distance between two particles is directly proportional to the diameter of the particles, assuming that the weight of quartz and the quantity of water in the quartz suspension remain constant.

This computation is also true for substances of different specific gravities and can also be applied, of course, to soil mixtures.

The area of soil particles, also compared with quartz, can be obtained as follows:

The weight of a quartz particle of spherical form with a radius $= r\mu$ is:

$$4/3\, r^3\, \pi \cdot 2.65 \cdot 10^{-12}$$

The number of quartz particles in 1 gm. of quartz is:

$$\frac{10^{12}}{4/3\, r^3\, \pi \cdot 2.65}$$

The area of 1 gm. of quartz is

$$\frac{4\, r^2\, \pi \cdot 10^{12}}{4/3\, r^3\, \pi \cdot 2.65}\, \mu^2 = \frac{3}{2.65\, r} \text{ square meters}$$

if r is expressed in μ.

If 2.65 is substituted by S as specific gravity in general, the formula obtains the general character:

$$A = \frac{3}{r\,s}$$

or, the area of the particles of quantities of a substance, equal in weight, is inversely proportional to the radius.

The effectiveness of difficulty soluble fertilizers, on one hand depends upon the area (speed of saturation and solution), and on the other hand upon the free distance between the particles (distance of diffusion).

THE ELECTRICAL CHARGE ON A CLAY COLLOID AS INFLUENCED BY HYDROGEN-ION CONCENTRATION AND BY DIFFERENT SALTS

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It is a well recognized fact that the physical condition of a soil depends to an important extent upon the colloidal state of the clay fraction, and it is of particular interest to learn how the reaction and the electrolyte content of the soil solution modify the state of dispersion of the clay. In such systems, one of the factors which is most effective is the electrical charge of the colloidal particles.[1] Recently Northrup and Cullen (8) have described an apparatus for measuring the cataphoretic charge of bacterial suspensions, and it occured to us that a similar procedure might be applied to a certain interesting colloidal clay, a supply of which was furnished to us by Prof. C. F. Shaw of the division of soil technology.

Since these experiments were completed, the writers have learned of the interesting investigations on cataphoresis and electric charge of soil colloids now being conducted by Bradfield (2), Mattson (7), Joffe and McLean (6), and Kelley[2] which will no doubt serve to develop this phase of soil colloid research. The present preliminary data are presented merely by way of suggestion, since they concern a very interesting, naturally occurring clay colloid and because the indirect as well as the direct effects of reaction on the cataphoresis of colloidal clay particles may be worth further discussion.

The clay employed in these experiments is described by Professor Shaw as follows:

Last spring in connection with the soil survey work in the Lancaster area, I had occasion to go over the recently dried surface of the big desert playa known as Lake Rosamund. The surface of this lake is entirely flat and at every inundation it receives an increment of very fine sediments. You will notice that over 95 per cent consists of clay particles less than 0.005 mm. in diameter. As I saw the undried material in the lake, it consisted of a gelatinous material that had settled out from the original solution, leaving the supernatant solution practically clear. As the material became drier, it attained a more or less jelly-like consistency and gave every evidence of being colloidal in nature.

An approximate chemical analysis of a water extract of this clay was made by Prof. P. L. Hibbard, with the following results:

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[1] It should be recognized, however, that the charge is not an inherent property of the colloidal particles, but may vary with the nature of the dispersing medium.

[2] Private communication.

Parts per million of dry material

	p.p.m.		p.p.m.
Ca	0	CO$_2$	420
Mg	0	HCO$_3$	1620
Fe	0	SO$_4$	2780
Na	5900	Cl	5600
		NO$_3$	positive test

In preparing the clay for the present studies, it was necessary to remove as far as possible all the soluble salts present. The clay was first sifted through a 200-mesh sieve, after which 40 gm. of the sifted material were shaken up thoroughly with 2 liters of distilled water. The suspension was then filtered in a Pasteur filter apparatus under pressure. Next the clay was scraped from the outside of the filter tube into a mortar, mixed with a little water, diluted again to 2 liters and shaken into a suspension. This suspension was titrated with 0.05 N HCl, with continuous shaking, until it came to equilibrium at approximately pH 5.0. The filtration through the Pasteur filter was repeated, residue again mixed with 2 liters of water and titrated with 0.02 N NaOH to pH 7.0 Finally the residue was washed six times with 2-liter portions of CO$_2$-free distilled water. The clay so prepared was made into a suspension according to the following procedure: About 10 gm. of the mud was mixed in a mortar with a little distilled water and this mixture was added to 3 liters of CO$_2$-free distilled water, the suspension shaken and filtered through a qualitative filter paper to remove any particles of sand or of organic matter. The filter paper was changed as soon as it started to clog. The suspension which passed through the filter paper was allowed to stand for 2 weeks, at the end of which time the heavier particles had settled out. These treatments yielded a translucent, amber colored suspension which was very stable. When viewed in a ray of sunlight, it had the dispersed appearance of a colloidal suspension. When coagulated by electrolytes a yellow, voluminous, jelly-like substance was precipitated. A portion of this suspension as finally prepared was tested qualitatively for the following ions: Ca, Mg, Cl, SO$_4$, Al, Fe and NO$_3$. A very faint trace of chlorine was found, but the other tests were negative. The specific resistance of the solution was approximately 935 ohms, and the pH value 8.5. It was found that the clay which settled out after long standing could be shaken up with more distilled water and a suspension formed which had the same conductivity, pH value and migration velocity as the original suspension. Obviously these treatments may have changed the chemical constitution of the original colloid, but for the purposes of this investigation, it was necessary to obtain a preparation freed as far as possible of di- and tri-valent ions and of contaminating salts.

A large number of preliminary experiments were made before it was found possible to develop a satisfactory technique for making the cataphoresis measurements. The apparatus employed was quite similar to that described by Northrup and Cullen, but several modifications were found advisable,

especially to provide stopcocks of as wide a bore as possible. It is quite probable, however, that a simplified form of a micro-cataphoresis apparatus would be more suitable for the purpose.

The clay suspension was supported in the cataphoresis apparatus on a 10 per cent sucrose solution, the latter being controlled so as to have practically the same electrolyte content and the same pH value as the suspension. The potential difference at the cell terminals was kept constant at 4 volts. The resistance of the saturated zinc sulfate in contact with the electrodes was considered negligible and since the distance between the 2 three-way stopcocks of the cell was 37 cm., the potential gradient was 0.108 volts per centimeter.

Each velocity measurement is computed as the sum of the distances over which the surfaces in two arms of the cell moved, one up and the other down, in a 10-minute interval. The measurements are expressed in terms of 0.5-mm. units, in which units the improvised cathetometer was calibrated. The accuracy of the measurements was dependent upon the exact control of conditions. Most important of all was the sharpness of the surfaces dividing the suspension and the sugar solution. Special comments are made later on the accuracy of individual measurements. The limiting error caused by mechanical difficulties and by bad surfaces was, in general, not greater than one-half of a velocity unit and was considerably less than this when sharp surfaces were obtained.

The pH values of the clay suspensions were always determined with the hydrogen electrode (Hildebrand type) and those of the sugar solutions were determined in some cases with the hydrogen electrode, and in other cases with the usual colorimetric methods. It was found impossible to determine the pH of the clay suspensions by the use of indicators, because of the remarkable combining or adsorbing capacity of this clay, which prevented the development of the normal color of the indicator.

EFFECT OF VARIATIONS IN pH ON THE VELOCITY OF MIGRATION OF THE COLLOID

In these experiments, in order to make negligible any effect of variations in total electrolyte content, NaCl was added to the suspension and to the sugar solution until both were of 0.01 N concentration with reference to this salt. Preliminary tests showed that at pH 8.5 (the pH of the suspension as prepared) and with NaCl present in 0.01 N concentration, the suspension travelled at a relative velocity of 6, and slight variations in the salt content did not produce any measurable change of velocity.

The clay suspension and the sugar solution to which NaCl had been added were each titrated to the desired pH values with a few drops of either 0.04 N NaOH or 0.04 N HCl as the case might be. After such addition of acid or of alkali, the conductivity of the solution was measured.

The velocity measurements at different pH values are given in table 1. It may be noted first that in every case the suspension travelled toward the

positive pole. There was no change in direction at any point between pH 2.1 and pH 12.7, which certainly covers the entire range found in soil solutions The velocity values from pH 5.0 to pH 10.0 are identical. At the extremes of acid or of alkaline reaction there was a decrease in velocity, but in these cases the cation concentration (H or Na) presumably became effective.

In the next experiments we made a series of velocity measurements for the purpose of determining the effects of various electrolytes in different concentrations. In every case the conductivity and pH values of the clay suspension and of the sugar solution were kept the same. The pH values of the suspensions were all 8.5, except when HCl, NaOH, $Ca(OH)_2$, Na_2CO_3, and $Al_2(SO_4)_3$ were used.

TABLE 1

Velocity of migration of clay colloid at different pH values

pH	RELATIVE VELOCITY	REMARKS
2.1	1	
2.4	2	Readings at pH 2.1 to 4.1 were not sharp
3.0	3	
4.1	5	
5.0	6	
5.4	6	
6.0	6	
7.0	6	
7.5	6	Readings at pH 5.0 to 10.0, inclusive, were sharp
8.5	6	
9.0	6	
10.0	6	
12.3	4	Readings at pH 12.3 and 12.7 were obtained with
12.7	0	difficulty

In all instances the suspensions migrated toward the positive pole. Every electrolyte used was effective in decreasing the charge of the suspension. The effective agent was primarily the positive ion, which is quite in accord with the fact that the suspension was negatively charged. The trivalent Al ion was most effective, followed by the H ion and the divalent Ca and Ba ions, and then by the monovalent Na and K ions. This order is, of course, the same as that usually obtained in colloid systems. With the higher hydrogen-ion concentrations, it remains to be determined whether the effect was produced by the hydrogen ions exclusively or whether other flocculating ions were brought into solution.

OTHER EXPERIMENTS

Clay suspensions which were washed with water until the electrolytes were reduced to a low concentration were found to have an increased velocity of

migration in the cataphoresis apparatus. This observation is confirmatory of the data already presented and is in agreement with other findings. Washing soils with distilled water nearly always tends to deflocculate them. Some years ago, Hoagland and Martin (5) observed that the withdrawals of solutes from the soil solution by growing barley plants caused significant changes in the amounts of material maintained in suspension when the soils were shaken up with distilled water. We may assume that the electrolytes present in the films surrounding the soil particles, as well as the nature of the latter, determine to a large degree the stability of the suspension.

A portion of the clay suspension was titrated very carefully with NaOH until complete coagulation was effected, care being taken not to add more NaOH than was necessary. The resultant mixture was then treated with an exactly equivalent amount of HCl and shaken into a suspension. The suspension so prepared was stable and did not coagulate on long standing. This

TABLE 2

Relative velocity of migration of clay colloid as influenced by different electrolytes

NaCl		Na₂SO₄		Na₂CO₃		NaOH		KCl		CaCl₂		Ca(OH)₂		BaCl₂		HCl		Al₂(SO₄)₃	
Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity	Concentration, milli-equiv.	Velocity
2.5	9	2.5	8	5.0	7	0.4	9	2.5	7.0	1.3	5	0.1	6	1.3	2	0.08	5	0.4	0
10.0	6	15.0	7	25.0	5	1.2	9	10.0	5.0	2.5	5	0.4	5			1.00	3		
20.0	5	30.0	5			20.0	4	20.0	4.5			1.2	5			4.00	2		
30.0	4	40.0	4			40.0	1	30.0	2.0							8.00	1		
40.0	2					60.0	0												
50.0	2																		

In all cases, the suspension migrated toward the positive pole.

experiment appears to show that for this clay suspension free from other electrolytes, NaOH had a greater coagulating effect than NaCl. It will also be noted from table 2 that NaOH had a greater effect in decreasing the velocity of migration than did NaCl. A similar experiment was carried out with Ca(OH)₂ and CaCl₂, and it was found that Ca(OH)₂ had a greater flocculating effect than CaCl₂.

The following experiment on the rate of settling was performed. To test-tubes, arranged in 6 rows, equal amounts of suspension were added. These different portions of the suspension were treated with successively increasing equivalent amounts of solutions of NaOH, NaCl, Na₂SO₄, Na₂CO₃, KCl, and CaCl₂, after which the tubes were thoroughly shaken and allowed to stand for 24 hours. The suspension had originally a pH value of 8.5 and all the solutions added, except those of NaOH and Na₂CO₃, were prepared so as to have the same pH values as the suspension. The divalent salt CaCl₂ showed by far the great-

est flocculating power. Among the monovalent electrolytes, the NaOH was considerably more effective than the others. KCl was next in order, but we did not find any significant differences in the flocculating powers of NaCl, Na_2SO_4, and Na_2CO_3. The general results of this experiment are entirely in accord with the determinations of the velocity of migration.

<div align="center">DISCUSSION</div>

Several years ago, O. Arrhenius (1) made the interesting suggestion that clay may act as an ampholyte and display a behavior analagous to that of proteins, in accordance with the explanation of Loeb. The clay used in these experiments presented a different type of behavior. The cataphoresis measurements did not yield any evidence that this clay colloid possessed a definite iso-electric point (in the sense that a protein has an iso-electric point) within the range of hydrogen-ion concentrations which permitted the formation of a stable suspension. It is possible that the experiments of Arrhenius may be susceptible of other interpretations, as indicated by Bradfield.

It is a very common observation that soils in contact with a highly alkaline solution, such as occurs in most so-called black alkali soils, show extreme deflocculation, and become very impervious to water. It does not necessarily follow, however, that the clay colloids are stabilized directly by the excess of hydroxyl ions. When the reaction of a soil solution is changed, it is obvious that the conditions governing the solution of a number of chemical elements are likewise changed. When the reaction becomes sufficiently alkaline, there will be a marked tendency for the concentrations of several strongly flocculating ions to decrease, whether as a result of chemical precipitation or some other type of removal from solution. For this reason, an alkaline reaction would promote stabilization even if the hydroxyl ion itself had no effect. However, with some colloidal clay preparations, an increased hydroxyl-ion concentration tends to accentuate the coagulating effect of the various cations. An example of this is what Comber (4) calls the abnormal flocculation produced by $Ca(OH)_2$. Comber's explanation of this abnormal flocculating power rests on the basis of the precipitation of a protective colloidal silica compound which is precipitated only when the reaction of the medium is alkaline.

In a recent article, Mattson (7) presents an interesting discussion of the flocculation of clay colloids and of other colloids. He also reaches the conclusion that calcium may have an enhanced effect under conditions of alkalinity but his explanation is somewhat different from that of Comber. Mattson advances the suggestion that adsorbed ions act as "Verbindungsglieder" between the colloidal particles. Two negatively charged particles may, perhaps, be held together by a positive ion such as calcium, and, under some circumstances, an alkaline reaction may increase the number of "Verbindungsglieder," and thereby hasten coagulation.

It is quite apparent that several different considerations are involved in any explanation of the effect of reaction on the coagulation of clay colloids. Certainly, as just stated, we must first give attention to the changes in the concentration of the multivalent cations in the medium, as related to the hydrogen-ion concentration, before we can decide whether or not the hydroxyl-ion has a specific dispersive influence. For example, when the solution is made alkaline, there may take place a precipitaion of calcium, magnesium, iron, or aluminum, as hydroxides, carbonates, silicates, or phosphates, and the removal of these very strongly flocculating ions from solution may tend to increase the dispersion of the colloid or its electrolyte requirement for univalent bases. A further addition of alkali, such as NaOH, may cause flocculation because of the influence of the sodium ions when they attain a sufficient concentration. On the acid side, the question of the effect of ions formed as a result of the solution of certain components of the clay, must not be overlooked. These ions, as well as the hydrogen ion, may promote flocculation. When neutral electrolytes are added to the system, we meet with the additional complication of the well known exchange of bases. On this account, the solution in equilibrium with the clay may be different from that which is added. Bradfield has emphasized the great importance of hydrogen-ion concentration in its effect on the liberation of bases from a clay colloid. A further question also arises with regard to the inherent colloid properties of the new silicate complex formed when sodium replaces other ions, as distinct from the effect of the ions present in the solution. It is possible that a critical analysis of the direct and indirect effects of hydrogen-ion concentration on the dispersion of clay colloids may clear up some of the apparent contradictions in the literature. It may be expected that the effect of hydrogen-ion concentration on the liberation of bases will vary with different colloid preparations.

Mattson made a number of micro-cataphoresis measurements on clay colloids, without special control of the exact hydrogen-ion concentration, but he found that the colloid was negatively charged under all the conditions employed. It would also appear that his general conclusion in regard to the effect of hydroxyl-ion concentration on the dispersion of the colloid is similar to our own, in which connection the following quotation (7) may be cited:

Die OH-ionen sind nicht an sich als die Bodenstructur beeinträchtigend zu betrachten. Die aufteilende Wirkung beruht vielmehr darauf, welche Kationen in der Bodenlösung überwiegen.

While it does not appear that clay possesses a definite iso-electric point in the same sense as a protein, it may still be possible for such a substance to show certain amphoteric properties when treated with strong acids or bases. The point which we wish to make now is that, within the range of reactions found in soil solutions, the clay colloid investigated by us showed no change in the sign of its electric charge, and the nature and concentration of the cations present in the solution had a predominant influence on the stability of the colloidal

suspension. Of course, in a soil other colloidal substances are present and these may not behave in the same way as the clay fraction. This would presumably be true of some of the organic colloids. Furthermore, Comber states that clay is readily flocculated by lime while fine silt is not.

A brief comment may be added concerning the bearing which the questions under discussion have on plant growth. It seems reasonable to assume that a highly alkaline reaction in the soil solution is unfavorable to the growth of most crops of agricultural interest. There are many reasons for this, including the direct effects of the increased alkalinity on root development, but the indirect effects are also of far-reaching importance. Not only may certain cations essential to plant growth be decreased in concentration to the detriment of the plant, but this same alteration on the soil solution may influence the physical state of the soil, and thus bring about a condition unfavorable to root development and to the activities of certain microörganisms.

SUMMARY

Measurements were made of the cataphoretic charge on a clay colloid as influenced by varying hydrogen-ion concentrations and by varying salts. It was found that the colloid remained negatively charged within the entire range of hydrogen-ion concentrations used (pH 2.1 to 12.7). The predominant factors determining the stability of the suspension were the nature and the concentration of the cations present in the medium. It is suggested that an alkaline reaction may sometimes cause deflocculation primarily because of the lessened solubility of di- and tri-valent cations, rather than because of the direct effect of the hydroxyl-ion concentration.

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THE DETERMINATION OF AMMONIA IN SOILS[1]

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A brief review of the literature on the determination of ammonia in soils indicates that there is no general agreement with reference to the best method. The object of this study was to investigate the errors involved in the determination, and the possibility of developing a more accurate method.

Potter and Snyder (6) investigated several methods and found that direct distillation of the soil with MgO causes liberation of some ammonia from organic nitrogenous compounds. They also found that complete recovery of ammonia which had been added to a soil could not be obtained by extraction with dilute HCl. They recommend the use of the Folin aeration method (2) with certain modifications, and indicate that good results were obtained when this method was used. The chief objection to this method is the time required.

Matthews (5) designed an aeration apparatus which shortens the time necessary for a determination but he found that in the case of some soils, complete recovery of ammonia added as $(NH_4)_2SO_4$ was not obtained.

Davisson (1) suggested a method by which the ammonia is obtained from soil extracts by very rapid aeration, using Na_2CO_3 and $Na_2C_2O_4$ to liberate the ammonia. The ammonia is first absorbed in a solution of H_2SO_4 and then the H_2SO_4 solution is distilled with MgO, in order to eliminate the error due to alkali being carried into the H_2SO_4 solution with the fine spray produced by the rapid current of air.

Gibbs, Neidig and Batchelor (4) modified the procedure recommended by Potter and Snyder by aerating the soil suspension for 1 to 1½ hours at a temperature of 75° to 85°C.

Valmari (8) recommended the use of a 0.5N NaCl solution for the extraction of ammonia from soils since he found that this treatment gives as much ammonia as is secured by dilute HCl extraction, and that the amount of organic nitrogen in most cases is much less in the salt extract than in the acid extract. Temple (7) has used a 1 per cent $CuSO_4$ solution to extract the ammonia from the soil. Both Valmari and Temple liberate the ammonia from the soil extracts by distillation with MgO.

EXPERIMENTAL

*The effect of hydroxyl-ion concentration on the liberation of ammonia from ammon-
ium compounds and the formation and liberation of ammonia
from organic nitrogenous material*

It is reasonable to believe that the action of the basic compounds in the
liberation of ammonia from ammonium salts and the formation and liberation
of ammonia from organic nitrogenous material is roughly proportional to the
concentration of the hydroxyl ions in solution.

The compounds which have been used by various investigators are given in
table 1. The hydroxyl-ion concentration of each of them has been determined
electrometrically and the data are expressed in terms of pH values.

Each of the compounds given in table 1 was added to 400-cc. portions of a
solution containing 10 cc. of 0.02N ammonium sulfate. It was found that
when $Ca(OH)_2$, K_2CO_3 and Na_2CO_3 were used all the ammonia was expelled

TABLE 1

Reaction of basic compounds

COMPOUND	STRENGTH OF WATER SOLUTION	pH VALUE
$BaCO_3$	Boiled suspension	9.00
$CaCO_3$	Boiled suspension	9.00
$MgCO_3$	Boiled suspension	10.00
Na_2CO_3	4 per cent	11.50
$Na_2CO_3 \cdot NaCl$	4 per cent Na_2CO_3 — 20 per cent NaCl	11.15
$Na_2CO_3 \cdot NaCl$	10.8 per cent Na_2CO_3 — 15 per cent NaCl	11.55
K_2CO_3	4 per cent	11.50
$K_2CO_3 \cdot KCl$	4 per cent K_2CO_3 — 20 per cent KCl	11.40
$Mg(OH)_2$	Boiled suspension	10.60
$Ca(OH)_2$	Saturated solution	12.60

in the first 100 cc. of distillate. It was necessary to collect 125 to 150 cc. when
using MgO, 175 to 200 cc. when using $MgCO_3$, and 300 to 350 cc. when using
$CaCO_3$ or $BaCO_3$. In all of these tests succeeding portions of the distillate
were nesslerized to determine when the evolution of ammonia was complete.

When 1 gm. of any one of the compounds given in table 1 was added to 500-
cc. portions of ammonia-free water containing 100 mgm. of any one of the fol-
lowing: acetamide, asparagine, alanine, cystine, glycocoll, guanidine car-
bonate, and "bacto peptone," it was found that amide nitrogen decomposed
very slowly at 100°C. when the pH value of the solution was 10 or less, but
that rapid decomposition occurred in solutions having a pH value higher than
10.5. At 42°C. under reduced pressure, amide nitrogen was stable in solutions
of pH 11.5 or less, while in solutions above pH 12 slow decomposition occurred.
Very little decomposition of amide nitrogen occurred when the various solu-
tions were aerated at room temperature with basic compounds which gave
pH values of 11.5 or less.

From these results it is evident that the ammonia can be secured from soil extracts either by distillation with $MgCO_3$ or by aeration with K_2CO_3 or Na_2CO_3 without any appreciable decomposition of organic nitrogenous matter. In testing several field soils it was found that practically the same result was secured when either MgO or $MgCO_3$ was added on distillation. This indicates the probable absence of amide nitrogen in normal soil extracts.

Extraction of ammonia from soil with salt solutions

Thus far it has been shown that ammonia can be completely liberated from a soil extract by distillation with MgO or $MgCO_3$ causing but slight decomposition of the organic matter. The chief difficulty, however, is to obtain by extraction all the ammonia which exists in the soil.

There are two ways in which ammonia may be held; namely, by adsorption and by chemical combination. It seems reasonable to believe that the addition of a salt of a strong base should increase the effectiveness of water in

TABLE 2

Ammonia extracted from a strongly acid soil

SOLUTION USED	AMMONIA EXTRACTED
5 per cent	*p.p.m.*
H_2O	5.25
$MgSO_4$	9.03
Na_4SO_4	13.20
$KC_2H_3O_2$	13.86
K_2SO_4	14.07
$CuSO_4$	15.96
KNO_3	16.80
$BaCl_2$	16.80

removing the ammonia from a soil by replacing the ammonia from insoluble ammonium silicates and also from that held by adsorption.

In order to find out how completely various salt solutions would replace the ammonia in soils, 50-gm. samples of a strongly acid soil and 250 cc. of various 5 per cent salt solutions were placed in pint jars and shaken in a mechanical shaker for 30 minutes. The suspensions were allowed to settle 10 minutes, were filtered on a Büchner funnel and 200-cc. portions of the filtrate were distilled with an excess of $MgCO_3$. The results given in table 2 are averages of closely agreeing duplicates. Shaking for 5 hours did not increase the amount of ammonia extracted.

More ammonia was secured from this soil by extraction with KNO_3 and $BaCl_2$ solutions than with any of the other salts used. Potassium nitrate does not form a precipitate on distillation and is much more desirable than $BaCl_2$ because all of the barium must be precipitated from solution before a sufficiently alkaline reaction can be secured to liberate the ammonia satisfac-

torily.   This requires the addition of a large amount of MgO or $MgCO_3$.   The heavy precipitate formed causes excessive foaming.   A large amount of magnesium salts also is produced which lowers the hydroxyl-ion concentration of the solution and results in a slower liberation of ammonia on distillation. This objection applies to all divalent and trivalent compounds such as those of calcium, copper, iron and aluminum.

In the next experiment, a study was made in regard to the completeness of the extraction of ammonia from several soils by means of a 5 per cent KNO_3 solution.   The ammonia content of the different soils was first determined by extraction with the salt solution.   Then a known amount of NH_4OH was

TABLE 3

Recovery of ammonia from different soils by extraction with a 5 per cent KNO_3 solution

SOIL USED	SOIL REACTION	AMMONIA IN SOILS	AMMONIA ADDED	TOTAL AMMONIA IN SOILS	TOTAL AMMONIA RECOVERED	RECOVERY OF AMMONIA ADDED
		p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*per cent*
Kewaunee silt loam..............	Very acid	18.17	33.6	51.77	51.57	99.1
Carrington silt loam..............	Acid	9.66	33.6	43.26	43.26	100.0
Plainfield sand...................	Acid	4.41	33.6	38.01	38.01	100.0
Raw peat.........................	Very acid	75.60	134.4	210.00	209.10	99.1
Decomposed peat.................	Neutral	45.30	134.4	179.70	179.70	100.0
Miami silt loam..................	Neutral	9.87	33.6	43.47	36.33	78.2
Black clay loam.................	Neutral	10.08	33.6	43.68	33.60	70.0

TABLE 4

Recovery of ammonia from soils by extraction with solutions of 8 per cent NaCl and 10 per cent KCl

SOIL AND REACTION	AMMONIA IN SOIL	AMMONIA ADDED	TOTAL AMMONIA IN SOIL	TOTAL AMMONIA RECOVERED		RECOVERY OF AMMONIA ADDED	
				NaCl solution	KCl solution	NaCl solution	KCl solution
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*per cent*	*per cent*
Miami silt loam neutral................	13.23	16.8	30.3	29.23	29.23	95.2	95.2
Carrington silt loam, acid..............	10.96	16.8	27.76	23.94	26.92	77.2	95.0

added to another sample of each of the different soils and another extraction made.   If this extract contained ammonia equal to the sum of the ammonia secured in the first extract and the ammonia added, the recovery of ammonia was considered 100 per cent.   As in the previous experiment 50 gm. of dry soil, or 12.5 gm. of peat, was used.   The results are given in table 3.

A rather low recovery of the ammonia was obtained from the Miami silt loam and the black clay loam by extraction with a 5 per cent KNO_3 solution. When the black clay loam was ground to pass a 200-mesh sieve and extracted with a 5 per cent KNO_3 solution, 80 per cent of the added ammonia was recovered.   When a 10 per cent KNO_3 solution was used, a recovery of 93.5

per cent of the ammonia added was secured. Since it is necessary to use a large amount of salt to completely extract the ammonia from some soils, a comparison of NaCl and KCl was made, using approximately equal molecular amounts of each salt. Fifty-gram samples of soil were shaken 30 minutes with 500 cc. of an 8 per cent solution in case of NaCl and a 10 per cent solution in case of KCl. It was found that NaCl and KCl were equally effective in the extraction of ammonia from a neutral soil, but in the case of the acid soil the KCl was more effective. The results are given in table 4.

In another experiment using two soils which had been incubated 7 days with 2 per cent of dried blood, it was found that a 10 per cent KCl solution (1 part soil to 10 parts of solution) extracted about 5 per cent more ammonia than a 10 per cent NaCl solution or a 5 per cent HCl solution. A 1 per cent $CuSO_4$ extract yielded about 5 per cent less ammonia than the 10 per cent NaCl extract. When these soil suspensions were aerated with K_2CO_3 the ammonia secured was from 1 per cent to 5 per cent more than that secured from the 10 per cent KCl extract. A 20 per cent KCl extract gave practically the same results as those secured by aeration.

Recovery of ammonia added to soil as ammonium hydroxide and ammonium sulfate

Potter and Snyder (6), Matthews (5), and Gibbs, Neidig and Batchelor (4) in order to test the efficiency of the aeration method, added ammonia as $(NH_4)_2SO_4$ to the soil before aerating. It was found in this investigation, using the aeration method, that ammonia added to a Miami silt loam soil as $(NH_4)_2SO_4$ could be recovered more completely than ammonia added as NH_4OH. The data are given in table 5. The rate of aeration was about 200 liters of air per hour. Tubes 1½ by 14 inches were used to hold the soil suspensions. Much better agitation was secured in the tubes than in Kjeldahl flasks.

When the ammonia added to this soil was determined by extraction with a 10 per cent KCl solution and distillation of the extract with MgO, 99 per cent of the ammonia added as $(NH_4)_2SO_4$ and 90 per cent of the ammonia added as NH_4OH were recovered. It is evident from these data and those given in table 5 that ammonia is more strongly absorbed by a soil when it is in the form of NH_4OH than when it occurs as $(NH_4)_2SO_4$. Therefore, in order to test the efficiency of a method for determining ammonia in soils, the ammonia should be added to the soil as NH_4OH, since ammonia and not ammonium sulfate is formed in the process of ammonification.

Comparison of extraction with potassium chloride and aeration methods

In these experiments comparisons were made using three different procedures, as follows: extraction of the soil with a 20 per cent KCl solution and distilling the extract with MgO; aeration of the cold soil suspension for 8 hours

with a solution containing 4 per cent K_2CO_3 and 20 per cent KCl; and aeration of the soil suspension at 75°C. with 2 per cent Na_2CO_3 solution (6).

The results of the first experiment are given in table 6. Complete recovery of ammonia added to these soils could not be secured with a 5 per cent KNO_3 solution.

The data given in table 6 agree with those given by Matthews (5) and show incomplete recovery of ammonia from some soils by the aeration method. When the same soils were extracted with a strong salt solution a satisfactory recovery of the ammonia added was secured in all but one case.

In the second experiment the ammonia content of a Miami silt loam soil was determined by the three different procedures. A 10 per cent solution of KCl was used instead of a 20 per cent solution as in the previous experiment.

TABLE 5

A comparison of the recovery of ammonia added to a soil as NH_4OH and $(NH_4)_2SO_4$, by aerating with a 4 per cent K_2CO_3 — 20 per cent KCl mixture

SOIL USED	AMMONIA ADDED	RECOVERY OF AMMONIA AT END OF			
		4 hours	8 hours	12 hours	22 hours
	p.p.m.	per cent	per cent	per cent	per cent
Miami silt loam...........	67.2 as NH_4OH	76	80	84.0	84.5
Miami silt loam...........	67.2 as $(NH_4)_2SO_4$	89.5	91		93.8

TABLE 6

Recovery of ammonia added to soils by aeration with a solution of 4 per cent K_2CO_3 and 20 per cent KCl and by extraction with a 20 per cent KCl solution

SOIL	AMMONIA ADDED	RECOVERY OF AMMONIA BY AERATION	RECOVERY OF AMMONIA BY EXTRACTION
	p.p.m.	per cent	per cent
Garden soil..................................	33.6	89.0	99.0
Alkaline peat................................	33.6	80.0	88.0
Alkali soil (California)........................	33.6	72.0	95.8
Alkali soil (California)........................	33.6	81.0	97.9

In order to determine if each of the different methods had completely removed the ammonia from the soil and also if the treatments involved cause an appreciable formation of ammonia from the decomposition of organic matter, the determinations according to the different methods were repeated several times successively on the same sample of soil. Ammonia-free water was added to the hot soil suspensions to replace that lost during each determination. The amounts of ammonia secured by extraction with KCl and by aeration of the cold soil suspension were nearly the same. Further extraction and aeration gave only very small additional amounts of ammonia. Similar results have been secured on a large number of soils.

When the Miami silt loam suspension was aerated at a temperature between 70 and 75°C., the amount of ammonia secured was almost twice as great as that secured by the other methods.   The total ammonia obtained by the second
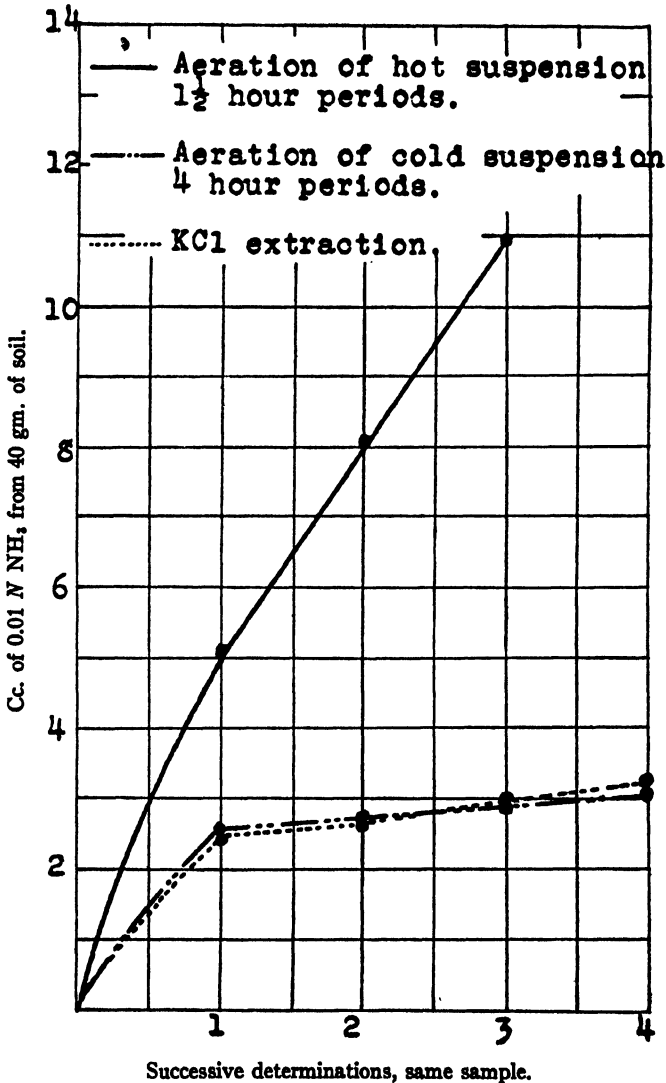
Fig. 1. Comparison of ammonia secured from a soil by successive determinations with different methods.

and third successive determinations by aeration at 75°C. was greater than that secured by the first determination, which indicates that there was considerable formation of ammonia from the organic nitrogen in the soil.   The results are plotted in figure 1.

The sharp break in the curves plotted from the data obtained by extraction and by aeration of the cold suspension, indicates that practically all of the ammonia was secured in the first determination. When the soil was aerated at a temperature of 75°C, it is evident that some organic nitrogenous matter was decomposed and ammonia produced as a result. This procedure is probably entirely satisfactory for ammonification experiments where large amounts of ammonia are secured, but it cannot be used for an accurate determination of the ammonia content of field soils which is usually very low.

Analytical procedure recommended

Pulverize and mix the soil thoroughly by passing it through an 8-mesh sieve. In case of dry soils, grind to pass a 60-mesh sieve. Weigh out 50 gm. of soil (12.5 gm. in case of dry peat) and place in a quart Mason jar. Add 500 cc. of a 10 per cent KCl solution (in case of neutral or alkaline soils use a 20 per cent KCl solution); shake for 30 minutes in a mechanical shaker; allow to settle 10 minutes and filter on a large folded filter. Transfer 400 cc. of filtrate to a Kjeldahl flask, add a small piece of paraffine to prevent foaming and a little 20-mesh limestone to prevent bumping. Distill with 1 gm. of MgO. Catch 125 cc. of distillate in 10 cc. of $0.02N$ H_2SO_4, boil to expel CO_2, cool and titrate with $0.02N$ NaOH using methyl red as an indicator. If the amount of ammonia is less than 2 mgm., nesslerization is recommended. Add 50 cc. of distillate to 2 cc. of Nessler's reagent, allow to stand about 5 minutes and compare in a nessler tube with standards made up at the same time containing from 0.1 to 0.6 cc. of 0.01 N $(NH_4)_2SO_4$.

In case of soil extracts from ammonification experiments, distill 250 cc. of the extract with 1 gm. of MgO and catch 125 cc. of distillate in 25 cc. of $0.2N$ H_2SO_4. Titrate the excess acid with 0.2 N alkali. In the case of soil extracts which contain large amounts of easily decomposable organic matter, 1 gm. of $MgCO_3$ may be used in place of MgO, 175 cc. of the distillate being then collected.

Discussion of analytical procedure

The above method has given satisfactory results both on field soils and in ammonification experiments. Soils treated with 10 per cent KCl solution can be shaken and allowed to stand over night without any change in ammonia content.

A filtered solution of commercial muriate of potash is recommended for use in the extraction of ammonia. Impurities such as magnesium salts are not objectionable.

Filter paper often contains small amounts of ammonia. These should be removed by boiling the paper in distilled water if small amounts of ammonia are to be measured.

Ammonia-free water can be readily prepared by redistilling ordinary distilled water to which has been added a little $KHSO_4$.

Nessler's reagent is prepared according to Folin (3) as follows: Dissolve 150 gm. of KI in 200 cc. of distilled water, add 200 gm. of HgI_2 and when this is in solution make up to 1 liter, filter and dilute to 2 liters. Add 750 cc. of this solution and 750 cc. of distilled water to 3500 cc. of 10 per cent NaOH prepared by dissolving 375 gm. of NaOH in 600 cc. of distilled water. Allow the carbonates to settle, decant the supernatant liquid and dilute to 3500 cc.

In case of neutral or alkaline soils a 20 per cent KCl solution is recommended to insure more complete extraction of the ammonia from the soil.

SUMMARY

A study of the various methods for determining ammonia in soils has been made. The pH values of the various compounds which have been used for the liberation of ammonia were determined. It was found that amide nitrogen decomposes slowly at 100°C. when the pH is 10 or less. If the pH is 10.5 or higher, rapid decomposition takes place at 100°C. At 42°C. under reduced pressure amide nitrogen is stable at pH 12 or less. These results show that ammonia can be secured either by distillation with magnesium carbonate or aeration with potassium carbonate without appreciable formation of ammonia from the decomposition of organic matter.

Various salt solutions were used to extract the ammonia from soils. It was found that a potassium chloride solution is the best for this purpose. Extraction with a 20 per cent potassium chloride solution gives practically the same amount of ammonia as aeration of a cold soil suspension containing 4 per cent potassium carbonate and 20 per cent potassium chloride. Aeration of a soil suspension at 75°C. containing 2 per cent sodium carbonate caused the formation of a considerable amount of ammonia from the organic nitrogen in the soil.

It was found that ammonia added to a soil as ammonium hydroxide was more difficult to recover than ammonia added in the form of ammonium sulfate.

A simple and rapid method was developed for the determination of ammonia in soils. A strong potassium chloride solution is used to extract the ammonia from the soil. The extract is then distilled with magnesium oxide to liberate the ammonia.

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ERRATA

Secular and Seasonal Changes in the Soil Solution, by John C. Burd and J. C. Martin
Soil Science, *vol. XVII, no. 2, August, 1924, p. 151–167*

Page 152, line 7 should read, "at *both* high and low moisture contents."
Page 152, footnote, should be "E. A. *Fisher*."
Page 153, in paragraph 3, line 7 should read "and *to* the portions."
Page 161, last line should read "soil *continues* to give."

The Availability of Nitrogen in Peat, by C. B. Lipman and M. E. Wank
Reference 12, p. 316, should read Waynick instead of Wayrick

DRYING OF SOIL, AS ONE OF THE NATURAL FACTORS IN MAINTAINING SOIL FERTILITY[1]

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During the last 25 years many authors have found that heating a soil to relatively low temperatures or treating it with weak antiseptics is accompanied by a marked increase in fertility. On one hand, this depends on the increase in solubility of some of the soil constituents, primarily organic nitrogenous compounds, and on the other hand on the change in the biological processes in the soil. It is well to point out in this connection the work of Dehérain, Demoussy, Richter, Russell and Ritter. Since the ordinary air-drying of soil also has a marked effect upon the solubility of nitrogenous constituents of the soil (analyses of our laboratory in 1910) and is capable of bringing about its partial sterilization, it seemed quite possible that the air-drying of soil should also manifest itself in an increase in its fertility. On the basis of the aforesaid, the problem has been studied during the years 1915 to 1920 in the chemical laboratory of the Shatiloff Agricultural Experiment Station. The results obtained have been published in the form of five communications in "The Experiment Station News" (2). The present paper represents the first general summary of the results obtained.

I

The experiments were conducted in the following way. The soil sample was taken in spring (April or May) from several places in a definite experimental plot. A depth of 3 or 4 vershoks[3] was sampled by means of a broad cylindrical auger, thus insuring a representative of the different depths of the plowed layer. The soil from the various borings was mixed, sifted through a $\frac{1}{10}$ mm. sieve to remove the roots and to insure better mixing; then it was separated into two equal parts. One part was left in the barn on a canvas, covered to diminish evaporation; the other was carried to the greenhouse, spread out in thin layers on iron sheets and left there exposed to light and air until completely dry. During sunny days this was accomplished in 1 or 2 days; in cloudy weather it required from 4 to 5 days. The dried soil was then placed in canvas bags

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[1] Translated from the Russian by Mrs. B. Trajkovich and J. S. Joffe, New Jersey Agricultural Experiment Station.

[2] Northern black soil district of Russia.

[3] A vershok equals 1.75 inches.

and moisture determinations made on it and also on the moist sample. In most cases the moisture content of the dry soil was found to be 3 to 6 per cent (on the basis of the absolutely dry substance); the moisture content of the moist soil varied from 25 to 35 per cent.

Each one of the soil samples was packed into Wagner glass or zinc pots with sand drainage and irrigation from below. In filling each of the pots sufficient dry or moist soil was taken to give equal amounts of absolutely dry soil. In order to obtain uniform packing, the wet and dry soils were moistened by mixing in pans with an amount of distilled water to make up a 35 per cent moisture content. From each of the samples taken in the field, four pots were made up: two with moist and two with dry soil.

The pots were then sown with millet[4] and watered daily so as to maintain an optimum moisture content equivalent to 33 per cent of the absolute dry weight of the soil (60 per cent of its total water-holding capacity). Watering was done with local well water, which, as shown by special experiments, scarcely raises the yield as compared with distilled water. When ripe, the millet was harvested, brought to a constant weight in special cupboards at the temperature of 60°C., weighed and thrashed by hand, after which the weight of the grain was determined.

During the years 1915 and 1918, when a general survey of the effects of drying was carried out, 81 samples from plots widely differing in their cultural condition were tested. During the year 1915, 2 samples were tested; during 1916, 18; during 1917, 58; and during 1918, 3 samples. On the basis of the yield of the wet soil sample as a check, the percentage increase or decrease in the yield of the dried soil sample, designated as the effect of drying, was obtained. Table 1 gives a summary of the results for 4 years.

It is evident that *the average effect of drying* in all experiments performed *is expressed in an increased yield* in the dried samples over the undried, amounting to 45 per cent for the total weight of crop, and 41 per cent for the grain alone. Besides, very large increases (127 per cent for the total weight and 123 per cent for grain) were obtained in 12 to 14 per cent of all the observations; medium increases (44 per cent for total weight and 44 per cent for grain) were found in 55 to 57 per cent of all the observations; small increases (10 per cent for total weight and 12 per cent for grain) were found in 22 to 24 per cent of all the observations; decreases in yield (2 per cent for total weight and 10 per cent for grain) were established in 5 to 11 per cent of all the observations. It is important to note that while the decrease in yield was expressed in most cases in insignificant figures of 2, 5 and 7 per cent, in the observations of large increases, doubling and trebling of yields occurred.

In this manner *in a large number of the observations the drying of the soil was accompanied by an increase in the yield of millet (also of oats and buckwheat) under the conditions present in the pot experiments.*

[4] In three cases buckwheat and oats were taken as plants for observation; however, since both of these plants, as it will be shown later, responded like millet to drying, the data have been compiled together.

TABLE 1

Increase in yield on dried soil samples as compared with undried

GROUPS ACCORDING TO THE MAGNITUDE OF THE EFFECT OF DRYING	AVERAGE EFFECT OF DRYING						NUMBER OF CASES				THE MAGNITUDE OF THE EFFECT OF DRYING FOR INDIVIDUAL CASES							
	Total for all groups		According to combination of groups		According to groups		In per cent		In absolute figures		On the basis of weight of grain				On the basis of total weight of yield			
	For grain	For total weight	For grain	For total weight	For grain	For total weight	For grain	For total weight	For grain	For total weight	1918 per cent	1917 per cent	1916 per cent	1915 per cent	1918 per cent	1917 per cent	1916 per cent	1915 per cent
<0			-10	-2	-10	-2	11	5	9	4	8	0,6,7,5,16,9,6,13		-33	10	2,0,5		-1
1-20			12	10	12	10	22	24	17	19	31	19,19,12,15,16, 14,9,4,13	19,13,13,4 11,10,8			1,7,9,13,8,4,17, 6,8,14,17	12,20,7,11, 18,1	
21-40	41	45	44	44	30	30	27	26	22	21		39,28,25,40,21,25, 29,30,39,31,29, 36,29	24,37,26,27, 29,33,30,34			39,39,33,26,26, 23,38,37,22,21, 32,40,30	30,28,33,23, 22,33,33,27	
41-60					49	49	17	24	14	20	66	41,49,50,56,56, 47,47,44,54,54, 50,44,51	47		45	44,43,53,58,55, 44,52,56,42,56, 42,58,57,45,44, 35,41	53,56	
61-80			123	127	67	72	11	7	9	6		68,61,67,67,67, 68,72,71				62,77,66,76,71,76		
81-100					91	88	5	5	4	4		86,96,95,86			83	98,86		87
>100					144	148	7	9	6	7		150,139,178	104,171	121		134,102,164,148, 183	105,203	

II

The soils used for the experiments without exception belonged to the experimental field of the station and therefore were genetically homogeneous, but, as already mentioned, they differed greatly in culture.

The station soil represents the middle-Russian tzernoziem of the northern half of the tzernoziem district with the following characteristic properties:

```
Depth of horizon A.................................................40 cm.
Depth of horizon B.................................................60 cm.
Humus.........................................................8–20 per cent
Total N.......................................................0.48 per cent
Total P₂O₅....................................................0.12 per cent
```

According to their previous cultivation, the soil samples used in the experiments may be classified under five main groups (for all groups plots were taken which had never received any manure or mineral fertilizers): (a) for many years a natural sod, (b) plots bearing perennial grasses, (c) plots sown year after year with the same plant, (d) plots subjected to a 3-year rotation and fallowing, (e) unsown plots kept continuously in fallowing. The effect of drying expressed in the percentage increase in yield of the dried samples as compared with corresponding undried samples, turned out to be as follows:

	TOTAL WEIGHT	GRAIN
	per cent	*per cent*
Uncultivated land (18 years)...............................	241	229
Two and three years' grass culture.........................	161	148
Continuous cropping with the same plant (5 to 6 years)........	138	133
Three-field rotations (fallow-rye-oats)......................	122	117
Continuous fallowing (3 to 5 years).........................	124	128

In the 3-field rotations besides the unfertilized plots, experiments with manured plots (2400 poods[5] three times in 18 years), phosphate (9 poods P_2O_5 two times in 6 years), and superphosphate (3 poods P_2O_5 two times in 6 years) were conducted.

The effect of drying on these plots was obtained as follows:

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                                                            per cent
Manured.............................................. ...........145–141
Fertilized with phosphate...........................................143–143
Fertilized with superphosphate......................................128–131
Unfertilized........................................................122–117
```

From the above cited figures it is evident that *the effect of drying is to a great extent dependent on the cultural conditions of the soil.* Besides: (a) The soils in an uncultivated condition appeared to be more sensitive to drying. (b)

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[5] One pood equals 36 pounds.

The same is observed in soils occupied by cultural perennial grasses, but to a somewhat smaller extent. (c) Soils under ordinary methods of tillage are less susceptible to drying and its effects depend but little on the rotation. (d) The application of manure and phosphoric acid increases markedly the effect of drying.

As already stated, the effect of drying is determined by the increase in yield as compared with the yield on the undried sample. Thus the magnitude of the effect is dependent upon the yielding capacity of the moist sample, and with two equal increases expressed in absolute figures, the lower the yield of the given sample in moist condition the greater will be the effect. If the effect of drying obtained from different samples should be correlated with their yielding capacity in moist condition (per cent)[6] then the results of the experiments during the years 1916 and 1919 may be represented by table 2. It is evident that *the effect of drying increases as the yielding capacity of the soil in moist condition decreases*, or in other words, the less fertile soils respond better to drying.

TABLE 2

Effect of drying on yielding capacity of soils

GROUPS ACCORDING TO THE MAGNITUDE OF EFFECT DUE TO DRYING	1916		1917	
	Average effect of drying	Average yielding capacity in moist condition	Average effect of drying	Average yielding capacity of soil in moist condition
per cent				
0–20	11	226	9	129
21–40	29	199	31	121
41–60	54	202	50	100
61–80			70	73
81–200	154	100	117	80

A closer examination of the cultural peculiarities of the soils which appeared to yield poorly in these experiments, allowed a characterization as soils potentially rich but capable of showing their fertility under special treatments only. These circumstances permit the conclusion that *drying is one of the powerful factors which help to transform the fertility elements of the soil from a potential to an active form*.

III

How do different plants respond to the drying of the soil? How does the effect of drying change with the degree of drying of the soil sample? How does repeated drying act? How do different horizons of soil behave in relation to drying? The above data, which showed the general significance of the drying phenomena, brought forth these questions, a solution of which would throw some light upon the subject.

[6] For each series of plots of *an experiment* the yielding capacity of one sample was taken as 100 and the yielding capacity of all the other plots was expressed in percentage of that sample.

Effect of drying on the yield of various plants

As has been pointed out the above figures were obtained almost exclusively with millet, and only an insignificant number of experiments have been carried out with oats and buckwheat. Since different plants respond very differently to soil fertility it was necessary to determine to what extent the increase in fertility under the influence of drying appears as a general phenomenon for different plants. An experiment was begun in 1917 as follows. One sample of soil was taken from the surface layer of a field in a 3-year rotation and, after

TABLE 3

Relative yields of various plants showing effect of drying the soil

PLANTS	YIELD ON MOIST SOIL	YIELD ON DRIED SOIL	AVERAGE EFFECT OF DRYING FOR DIFFERENT CROPS
Meadow plants..................................			329
Gold hammer...............................	100	568	
	100	291	
Legumes..			35
Shabdar...................................	100	138	
Red clover................................	100	137	
Vetch.....................................	100	135	
Lentils....................................	100	134	
Alfalfa....................................	100	131	
Field crops....................................			28
Corn......................................	100	137	
Oats......................................	100	130	
Wheat (summer)...........................	100	130	
Millet.....................................	100	117	
Root, tuber and oil-yielding plants..............			11
Sunflower.................................	100	116	
Beets.....................................	100	112	
Carrots...................................	100	111	
Flax......................................	100	109	
Potatoes..................................	100	108	

a suitable preparation similar to that described above, was packed into pots which were then sown with 16 different plants, 4 pots being assigned for each plant—2 with moist soil and 2 with dried. The experiment gave the results shown in table 3.

All cultivated plants of the locality responded to drying with the following outstanding results: (a) The meadow plants showed an especially strong response, trebling and quadrupling the yield under the influence of drying. (b) Leguminous and field crops responded well to drying, the former more strongly than the latter. (c) Root, tuber and the oil-yielding plants showed a weak response, especially those that are cultivated during the growing season.

It is worth while to note that the greatest response has been obtained with plants which under natural conditions thrive in soils not subjected to the drying influence in tilling operations (meadows); the least response, on the contrary, was obtained with cultivated plants exposed to the greatest artificial drying caused by cultivation in the row.

Degree of drying for beneficial effects

The degree of drying under which the above effects have been obtained resulted, as mentioned, in 3 to 6 per cent moisture. The question arose

TABLE 4

Relative yielding capacity showing effect of degree of drying

SOIL	MOISTURE AS COMPARED WITH ABSOLUTELY DRY SUBSTANCE	TOTAL WEIGHT	GRAIN
	per cent		
3-year system......................	32	100	100
	23	81	81
	13	94	91
	9	96	94
	6	131	127
	3	135	129
4 years of fallow.....................	37	100	100
	25	75	73
	15	73	73
	9	91	83
	6	136	135
	3	144	151
Sod for 18 years.....................	34	100	100
	23	83	88
	14	111	114
	7	217	229
	3	248	239

whether it is necessary to reach that degree of moisture and how in general does the fertility of the soil vary under different conditions of drying.

An experiment was set up in 1917 as follows. The sample of moist soil under experimentation was tested for its moisture content, then it was spread in thin layers on iron sheets and dried in the air to the weight which would correspond to the required moisture content. During the process of drying the soil was stirred almost continuously in order to avoid uneven drying of the upper layers. All samples described below were treated in this manner. Three samples of soil were taken for the investigation: (a) from a field under cultivation according to the old 3-year system, (b) from a field in fallow for 4 years, (c) from a field in sod for 18 years. The plant used in the experiments

was millet. The numbers in table 4 showing the greatest moisture content belong to the moist samples, which have not been subjected to ing, their respective yields being taken as 100.

It appears that *a positive influence of drying soils subjc* cchanical *treatment, starts only at a 6 per cent moisture content, and for :* d land at *14 per cent. A decrease in yield is observed during the first st* ing.

Effect of repeated drying on yield

Repeated drying also was investigated. The soil sample was divided into five parts. The first part was left moist, and the others were subjected to drying. The second part was dried once, the third part after ti irst lrying was moistened again with distilled water up to its original weight an' then dried again; the fourth part was dried the same way 3 times; and the fiftth part 4 times. All samples were then made up to the same moisture content and packed into pots. The plant used was millet. Three samples of soil were taken for this investigation: one from a field under the old 3-field system which has never been fertilized; another from the same kind of field but which

TABLE 5

Relative yielding capacity showing effect of repeated drying

SOIL	TOTAL WEIGHT				
	Moist	Dried once	Dried twice	Dried 3 times	Dried 4 times
3-field system unmanured................	100	145	137	154	156
3-field system manured...................	100	110	169	181	144
Uncultivated land......................	100	183	212	222	219

had been manured; the third from a field uncultivated for 18 years. The results are shown in table 5.

Repeated drying increases fertility of the soil still further, and the maximum effect is apparently obtained with triple drying.

Effect of drying on the yield of different horizons

An experiment to ascertain the response to drying of the different horizons of the soil was set up in 1917 with three soil samples; from a field under the old 3-field system which has never been manured; from a plot 4 years in fallow; from a field uncultivated for 18 years. In each one of these fields two borings were made to the depth of 1 meter and layers of soil were taken from the walls of these holes at 0 to 20, 20 to 40, 40 to 60, and 60 to 80 cm. In the four borings on the plot of the 3-field system and in the uncultivated field horizon, *A* ended at 42 to 45 cm; and horizon *C* began at 1 meter; in two borings on the fallowed field, horizon *A* ended at 20 cm., and horizon *C* began at 63 cm. Layers of soil from duplicate borings were combined and passed through a sieve. Half the combined sample was dried; then the packing of wet and dry

soil was carried out according to the methods described.   The plant used was millet.   The results obtained are shown in table 6.   The yields from the dried samples are expressed in the percentage of yield from the corresponding moist samples.

The maximum effect of drying was exhibited by the two middle horizons, 20 to 40 and 40 to 60 cm.   It decreased in the upper layer (0 to 20 cm.) as well as in the lower (60 to 80 cm.).   This phenomenon is undoubtedly connected with the periodic drying through the cultivation of the upper layer; the decrease in humus content and in the number of microörganisms which always occur in regions of transition to the subsoil, is responsible for the phenomenon in the lower layer.   This view is supported by the absence in the case of the sample from the fallow field, where the horizon 60 to 80 cm. was already the subsoil. It is worth while to pay special attention to the great difference between the cultivated and the uncultivated soils, although the borings from which the samples were taken were not more than 10 sajens[7] apart.   Apparently the uncultivated land differed greatly from the cultivated land as far as the distribution of organic substances and microflora is concerned.

TABLE 6

Effect of drying on yield of different horizons

(Per cent of yield of moist samples)

HORIZONS	0 TO 20 CM.	20 TO 40 CM.	40 TO 60 CM.	60 TO 80 CM.
Field under the old 3-field system.............	141	288	259	140
Field under 4 years' fallow....................	176	314	273	96
Uncultivated land...........................	283	374	374	282

IV

The tremendous effect of drying found in all described experiments apparently must be accompanied by some appreciable changes in the composition of the dried soil.   In order to determine the nature of the changes and their significance, analyses of three samples of soil in moist and dried condition have been carried out, as follows:

cm.

Cultivated land, horizon... 0–20
Cultivated land, horizon...20–40
Uncultivated land, horizon... 0–20

Soil extracts were prepared and analyses made for the total minerals, organic substances, nitrogen and P_2O_5 in the extract.   The solvents used were water, 2 per cent acetic acid, 2 per cent citric acid, 0.5 per cent oxalic acid, 0.5 per cent nitric acid, and 1 per cent nitric acid.   Besides, the total amount of ammonia, amides and bacterial numbers in the soil were determined.   The extracts were obtained by shaking the soil for $\frac{1}{2}$ hour with five times its amount of the

[7] 1 sajen equals 7 feet.

solvent.   The amount of water contained in the soil was taken into con~~~~leration in calculating the strength of the solvent.

Determinations of the mineral substances were carried out by evaporating a certain amount of the sample, igniting and treating the residue with HNO_3.

Determinations of the organic substances were carried out by the permanganate method modified in the author's laboratory.   The total nitrogen was determined (according to Kjeldahl) by digesting a certain amount of the extract after acidifying the sample and evaporating almost to dryness in the Kjeldahl flask on a water bath.

The organic matter having been removed with $KMnO_4$, total phosphorus was determined by a colorimetric method worked out in the author's laboratory.

Ammonia nitrogen was determined by Schloesing's method modified in the author's laboratory, extracting the soil with oxalic acid and distilling the extract with MgO.

Amide nitrogen was determined by *Bussen's* method, by distilling a certain weight of soil with MgO.   Finally the number of bacteria was determined by the ordinary bacteriological methods with Brown's albumin agar as the nutrient media.

The results obtained are compiled in table 7.

The table shows that the analyses do indicate large chemical changes taking place in the soil upon drying.

It is necessary to note here: (*a*) the small change in the solubility of mineral substances, (*b*) large increase in the solubility of organic substances, (*c*) large increase in the two fundamental nutrient substances, nitrogen and phosphorous, (*d*) an extremely large increase in the soil of ammonia nitrogen, (*e*) a considerable increase in the amide nitrogen, and (*f*) a sharp decrease in the number of microörganisms.

All the changes are similar to those which take place in the soil under the influence of partial sterilization with antiseptics or by heating, a phenomenon observed earlier by various authors.   Therefore, according to the character of the chemical changes, we are obliged to consider drying of soil as its partial sterilization.

Let us pay some attention to some of the relationships resulting from the data.   (*a*) The weaker the solvent taken for extraction, the more pronounced is the difference between the moist and dried soil; the 1.0 per cent nitric acid does not in many cases make any more difference.   (*b*) In regard to chemical analysis, the soils correspond in order to the yielding capacity in the pots.   (*c*) *the analyses of a soil for its fertility cannot be made on a dried sample; this probably explains the failure of such analyses.*

<center>V</center>

The similarity in the chemical changes taking place in the soil under the influence of drying, with those after partial sterilization, induced the author to determine the influence of partial sterilization on the soil used in the experiments on drying.

TABLE 7

Composition of soil extracts with various solvents

(Per kilogram of dry soil)

		CULTIVATED, 0 TO 20 CM.		CULTIVATED, 20 TO 40 CM.		UNCULTIVATED, 0 TO 20 CM.	
		Moist	Dried	Moist	Dried	Moist	Dried
		mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
Total mineral substances	Water	235	200	110	175	165	170
	Acetic acid	3,260	3,650	2,860	3,470	3,080	3,760
	Citric acid			6,230	6,990		
	Oxalic acid	2,620	2,520	2,870	3,220	2,140	1,670
	Nitric acid, 0.5 per cent			8,940	10,050		
	Nitric acid, 1.0 per cent	14,090	14,160	13,250	12,640	13,040	13,340
Total organic substances	Water	36	120	0	444	51	301
	Nitric acid, 0.5 per cent			650	1,237		
	Nitric acid, 1.0 per cent	460	596	1,172	1,698	957	1,086
Total nitrogen	Water	14.5	16.7	8.5	38.1	7.2	23.3
	Acetic acid	34.2	36.3	10.6	51.0	17.3	24.8
	Citric acid			17.5	70.5		
	Oxalic acid	50.1	56.7	25.9	64.3	18.8	35.4
Total P_2O_5	Water	1.2	2.5	0.7	4.7	0.6	7.2
	Acetic acid	2.6	4.6	3.0	7.0	2.3	6.0
	Oxalic acid	59.1	57.9	71.6	73.7	37.9	37.7
	Nitric acid, 0.5 per cent			16.6	19.1		
	Nitric acid, 1.0 per cent	39.7	41.1	41.4	41.9	22.5	23.4
Ammonia nitrogen		0	14.300	1.000	14.600	0.210	24.300
Amide nitrogen		61.400	93.900	38.500	64.000	75.800	88.500
Number of bacteria (millions per gram)		1.650	0.380	0.920	0.201	1.955	0.702

TABLE 8

Effect of sterilization on crop yield

	LOW SMALL ZINC POTS		HIGH SMALL GLASS POTS	
	Unsterilized	Sterilized	Unsterilized	Sterilized
Total weight of yield	100	248	100	411
Grain	100	254	100	700

In 1919 the author tried to establish the influence of steam sterilization in an autoclave at 2 atmospheres' pressure for 4 hours. A soil from one of the rotation plots of the experiment station fields, after sterilization, was packed into pots and sown with spring wheat.

The influence of sterilization was very great, the increases obtained being the greatest known in literature. The black soil of the experimental station

may be characterized, therefore, as one that is very sensitive to such treatments.

The influence of somewhat weaker reagents was tested in 1917; the treatments consisted in heating to different temperatures at ordinary pressure, and the use of antiseptics. The soil was taken from the field in the old 3-field system which had not received any fertilizers. The heating was performed in receptacles on a water bath soon after the sample with its natural moisture content was taken; the period of heating was 7 hours from the time the soil assumed the required temperature. The treatment with antiseptics was carried out in glass flasks filled to half their capacity with soil. Into the flasks wire spirals filled with cotton and wrapped with cloth were placed, the cotton being soaked with the antiseptic; the soil was subjected to the fumes of the antiseptic for 3 days, during which time it was frequently mixed by shaking and rolling. Chloroform, toluol and formalin were the antiseptics used. At the end of the period, the soil was placed on iron sheets for ventilation, precautions being taken against drying; the ventilation was carried out in a dark

TABLE 9

Relative yields showing the effect of heating and antiseptics on the yielding capacity of soils

	USUAL TEMPERATURE		HEATING							ANTISEPTICS		
	Moist	Dried	35°C.	45°C.	55°C.	65°C.	75°C.	85°C.	95°C.	Chloroform	Toluol	Formalin
Total weight..............	100	117	93	121	135	158	142	150	180	170	164	97
Grain......................	100	107	86	115	126	147	119	128	161	165	142	79

cool place; the weight of water lost by evaporation was compensated by spraying the soil with distilled water. It took 3 days to removed the chloroform or toluol; and, more than a week to remove the formalin (even then the odor could be detected). The soils were packed into pots with ordinary precautions, and sown with millet.

The experiment (table 9) showed, that *antiseptics or moderate heating influenced the fertility of the soil very greatly, exceeding in that respect the influence of drying.*

A very interesting phenomenon represents the disproportionately high increase in yield at 65°C., and its decrease at 75°. This is observed to be in perfect analogy with the course of evolution of CO_2 in the heating of soil as established by Dehérain and Demoussy (1). They obtained an increase in the evolution of CO_2 from 45° to 65°, a decrease from 65° to 80° and another rapid increase above 80°. This may be explained by considering the combined action of the biological and chemical oxidation at low temperatures, the disappearance of the biological factor at temperatures above 60°, and an increased chemical decomposition at temperatures above 80°.

VI

Whether the drying of soil is carried out under artificial conditions or takes place under natural conditions in the surface horizon of the field, the phenomenon of drying is a result of several reciprocally related factors. Outside of the removal of water by evaporation, other things take place, such as: an increased aeration of the soil and subsequently the influence of oxygen; the heating caused by the sun rays which, in the case of the black-soils, reaches very high temperatures; the effect of the light itself which is capable of influencing the biological processes of the soil as well as its chemistry.

The question therefore arises, as to which of the four factors instrumental in the drying of soils should the main rôle of increasing the soil fertility be ascribed; the removal of water, the increased aeration, heating, or the influence of light?

TABLE 10

Influence of aeration in connection with drying of soil, 1917

	CULTIVATED LAND, UNFERTILIZED			
	Ordinary moist	Dried	Spread out and watered	Anaerobic
Total weight.............................	100	117	95	84
Grain......................................	100	107	95	83

TABLE 11

Influence of aeration and various degrees of moisture in connection with drying

1918, TOTAL WEIGHT	ORDINARY MOIST	DRIED	AERATION IN DARKNESS	ANAEROBIC
Cultivated but unfertilized....................	100	145	129	93
Cultivated and manured......................	100	110	85	73
Uncultivated...............................	100	183	125	108

Two experiments during 1917 and 1918 were intended to throw some light on the influence of aeration. The soil samples, taken from the surface horizon of the different plots, after having been passed through a sieve and well mixed, were divided into equal parts and subjected to the following treatments. One part was placed in glass flasks, stoppered and kept in darkness in an anaerobic condition without excess of oxygen; the second part was spread out in a thin layer on an iron sheet, placed in a dark barn and kept at a constant moisture content; the third part was spread in thin layers on an iron sheet, placed in the green house and exposed to drying; the fourth was left in the barn in a pile. The results showing the yield in relative numbers are given in tables 10 and 11.

Anaerobic preservation in all cases except in the uncultivated land gave a decrease in yield; aeration in darkness in two cases produced small decreases

in yield, and in two others small increases; drying in sunlight, that is to say, combined action of dehydration and aeration caused by the heat and light, gave in all cases considerably larger yields than all other preliminary treatments. In that way it has been established, *that aeration by itself, even if it does raise the yield, does it to an insignificant extent;* and in the same way *exclusion of oxygen decreases the yield insignificantly. A large effect is produced by drying in sunlight only, that is to say, the combined action of dehydration due to the sun rays, the light itself and aeration.*

In 1921 the author attempted to separate out completely each of the named factors.

The scheme was as follows:

    I. Maintaining anaerobic conditions without drying.
    II. Maintaining aerobic conditions without drying.
    III. Maintaining aerobic conditions with drying.

In each series, the preparation of the soil was carried out:

    (*a*) at ordinary temperatures in darkness.
    (*b*) at raised temperature in darkness.
    (*c*) in reflected light.
    (*d*) in the sunlight.

The setting up was carried out in the following way.

Anaerobosis was attained by placing soil in glass carboys of 5 poods capacity. These were stoppered with corks and sealed with Mendeleeff's sealing wax. Some of the carboys were then placed in an absolutely dark place at ordinary room temperature; a second group, in a dehydrating oven, kept in darkness and heated to a certain temperature; a third, in a greenhouse with glass roof; a fourth, in the same greenhouse under immediate sun rays.

Aerobic conditions without drying were attained by spreading the soil in a thin layer on iron sheets, with continuous stirring and watering from a spray thus keeping it at constant weight. As far as the temperature and light are concerned the conditions were the same as in the preceding case.

Aerobic conditions with drying were attained in the same way as the preceding; beside the moistened soil was a sheet with unmoistened soil.

In the course of the experiment the sun was very hot and the differences were therefore especially marked.

The temperatures of the places of storage were as follows:

The dehydrating oven...38–42°C.
The greenhouse in the sun...29°C.
The greenhouse in dim light...25°C.
The ordinary room temperature.......................................20°C.

The length of treatment under different conditions was naturally very different and is indicated in the following figures:

days
Anaerobic in sunlight...10
Anaerobic in reflected light...10
Anaerobic in darkness at ordinary temperature..............................10
Anaerobic in darkness at rising temperature................................10
Aerobic in sunlight... 2
Aerobic in reflected light... 4
Aerobic in darkness at ordinary temperature...............................10
Aerobic in darkness at rising temperature.................................10

Two samples of soil were taken, layer 20 to 40 cm. from an old cultivated land which has never been manured, and layer 0 to 20 cm. from uncultivated land.   At the end of the treatment the soil was packed into pots and sown with millet.   Table 12 shows the data of yields:

In order to single out the various interesting factors which these data afford, the conclusions in tables 13 and 14 may be drawn.

The influence of oxygen on uncultivated soils in all cases was found to be negative, on cultivated soils in two cases negative and in one case positive;[8] on the average, in the case of the uncultivated soil, 21.4 per cent, and for cultivated soil, 4.4 per cent.   In other words, oxygen either has no effect or its effect is negative.

The removal of the water caused a large increase in yield on the uncultivated as well as on the cultivated soil.

The influence of raised temperatures (table 15) was revealed on both soils in a large increase in yielding capacity, for uncultivated land in 154 per cent, for cultivated in 60.9 per cent.[9]

Since the influence of light is always complicated by the simultaneous increase in temperature, this appeared to be the most difficult question for solution.   The three gradations of light used in the experiment are accompanied by the following differences in temperature: darkness, 20°; reflected light, 25°; sunlight, 29°.   Because of that, in tables 16 and 17 besides the direct relationships of the different gradations of light, the data with the increase due to temperature are given, the latter having been calculated arbitrarily according to the above figures of the influence of the raised temperature: for the fallowed land 3.0 per cent per 1° (60.9: 20 = 3°), for uncultivated land 7.7 per cent per 1° (154: 20 = 7.7).

From tables 16 and 17 it is evident that the effect of light on cultivated land has been clearly negative; even without corrections for the temperature in all of the averages, in most of the individual cases the results obtained have been negative.   For uncultivated soil increases in yield have been obtained without corrections for temperature, which is easily explained by the fact that this soil is highly reactive to heating.   It is actually true that when the corrections for

[8] The fourth pot was discarded, for since the duplicate pot of the series, "darkness at ordinary temperature anaerobic," was broken, the remaining gave a foreseen decreased yield.

[9] The increase of 200 per cent was disregarded, because in calculating, the same doubtful figure 0.8 as above was used.

TABLE 12

Total weight of yield showing the effect of light at various temperatures in connection with drying of soils

	ANAEROBIC WITHOUT DRYING				AEROBIC WITHOUT DRYING				AEROBIC WITH DRYING			
	Darkness at ordinary temperature	Darkness with temperature raised	Reflected light	Sunlight	Darkness at ordinary temperature	Darkness with temperature raised	Reflected light	Sunlight	Darkness at ordinary temperature	Darkness with temperature raised	Reflected light	Sunlight
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
Old cultivated land.........	(0.8)	2.4	1.4	1.2	1.5	2.2	1.1	1.4	2.8	4.9	2.9	2.1
Uncultivated land..........	1.5	4.3	1.4	2.0	1.4	3.0	1.0	1.6	1.8	4.7	2.4	2.0

TABLE 13

The influence of oxygen

SOIL	CULTIVATED				UNCULTIVATED			
	Total weight		Increase due to oxygen		Total weight		Increase due to oxygen	
	Without oxygen	With oxygen			Without oxygen	With oxygen		
	gm.	gm.	gm.	per cent	gm.	gm.	gm.	per cent
Darkness at ordinary temperature..............	0.8	1.5	(+0.7)	(+87.0)	1.5	1.4	−0.1	−6.7
Darkness with temperature raised...................	2.4	2.2	0.2	−8.4	4.3	3.0	−1.3	−30.2
Reflected light.............	1.4	1.1	−0.3	−21.4	1.4	1.0	−0.4	−28.6
Sunlight...................	1.2	1.4	+0.2	+16.7	2.0	1.6	−0.4	−20.0
Average.................				−4.4				−21.4

TABLE 14

The influence of the removal of water

	CULTIVATED				UNCULTIVATED			
	Total weight		Increase due to drying		Total weight		Increase due to drying	
	Without drying	With drying			Without drying	With drying		
	gm.	gm.	gm.	per cent	gm.	gm.	gm.	per cent
Darkness at ordinary temperature...................	1.5	2.8	+1.3	+86.9	1.4	1.8	+0.4	+28.5
Darkness with temperature raised...................	2.2	4.9	+2.7	+123.5	3.0	4.7	+1.7	+56.7
In reflected light.............	1.1	2.9	+1.8	+164.0	1.0	2.4	+1.4	+140.0
In sunlight.................	1.4	2.1	+0.7	+50.0	1.6	2.0	+0.4	+25.0
Average.................				+105.9				+62.5

temperature are introduced the increases in yield are changed into decreases. One might think that light in itself does not play any rôle in the increased fertility in soil drying and apparently has even a negative effect.

TABLE 15

The influence of rise in temperature

	CULTIVATED				UNCULTIVATED			
	Total weight		Increase due to temperature		Total weight		Increase due to temperature	
	Ordinary temperature, 20°.	Raised temperature, 40°.			Ordinary temperature, 20°.	Raised temperature, 40°.		
	gm.	*gm.*	*gm.*	*per cent*	*gm.*	*gm.*	*gm.*	*per cent*
Anaerobic without drying.......	(0.8)	2.4	(+1.6)	(+200.0)	1.5	4.3	+2.8	+186.5
Aerobic without drying........	1.5	2.2	+0.7	+46.7	1.4	3.0	+1.6	+114.0
Aerobic with drying............	2.8	4.9	+2.1	+75.1	1.8	4.7	+2.9	+161.5
Average....................				+60.9				+154.0

TABLE 16

The fundamental data

	INCREASE					
	Reflected light, temperature, 25°; darkness at ordinary temperature, 20°		Sunlight, temperature, 29°; reflected light, temperature, 25°		Sunlight, temperature, 29°; darkness at ordinary temperature, 20°	
	gm.	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*
Cultivated						
Anaerobic without drying.......	(+0.6)	(+75.0)	−0.2	−14.2	(+0.4)	(+50)
Aerobic without drying.........	−0.4	−26.7	+0.3	+27.2	−0.1	−6.7
Aerobic with drying............	+0.1	+8.6	−0.8	−27.6	−0.7	−25.0
Average....................		−7.7		−4.9		15.8
Uncultivated						
Anaerobic without drying.......	−0.1	−6.7	+0.6	+43.0	+0.5	+33.3
Aerobic without drying.........	−0.7	−50.0	+0.6	+60.0	+0.2	+14.3
Aerobic with drying............	+0.6	+33.3	−0.4	−16.7	+0.2	+11.1
Average....................		−7.8		+28.8		+19.6

A summary of all the data on the effect of the individual factors in the drying of soil is presented in table 18.

It may be that in all cases the removal of the water and the increase in temperature give a positive effect; and the oxidation with oxygen, with the aid and the influence of light, negative. In one case, the removal of the water acts

more strongly than the increase in temperature; in the other the action of temperature is stronger than the increase in dehydration.

Therefore we can say that the change in fertility of the soil by drying is conditioned by the *removal of water*, by evaporation, and by the heating of the soil by the rays of the sun.

TABLE 17

Summary of the effect of light in connection with drying of soils—average of the results

	CULTIVATED			UNCULTIVATED		
	Reflected light, darkness	Sunlight, reflected light	Sunlight, darkness	Reflected light, darkness	Sunlight, reflected light	Sunlight, darkness
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Without correction for temperature..........	−7.7	−4.9	−15.8	−7.8	−28.8	−19.6
With correction for temperature..............	−22.7	−16.9	−42.8	−46.3	−0.2	−49.7
Average { Without corrections..............	−9.4			−13.5		
With corrections.................	−27.4			−32.7		

TABLE 18

The increase in yield under the influence of the individual factors

	CULTIVATED					UNCULTIVATED				
	Darkness at ordinary temperature	Darkness with temperature raised	Reflected light	Sunlight	Average	Darkness at ordinary temperature	Darkness with temperature raised	Reflected light	Sunlight	Averages
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Oxygen		−8.4	−21.4	+16.7	−4.4	−6.7	−30.2	−28.6	−20.0	−21.4
Water	+86.9	+128.5	+164.0	+50.0	+105.9	+28.5	+56.7	+140.0	+25.0	+62.5
Temperature		+40.7 +75.1			+60.9		+186.5 +114.0 +161.5			+154.0
Light			+22.7	−16.9 −42.8	−27.4			−46.3	−0.2 −43.7	−32.7

VII

All of the above data have been obtained under artificial conditions; the soil sample which was taken from the field was dried in the air and its fertility was determined by means of pot experiments. Does the above-named process take place under natural conditions and what are the results accompanying it? An approach to this problem was made in three ways.

First, observations were taken on the moisture content of the surface layers of the soil under natural conditions.   Samples were taken from the experiment station fields in the following way.   From each place dry lumps of soil were collected and then the wet ones lying next to them or right underneath; their moisture content was then determined.   Data on the collected material is compiled in table 19.

The data which have been taken as representative from many others show, that *the drying under natural field conditions may reach a very high degree: sufficient, as we have seen, to cause large increases in soil fertility*.   It takes place under the influence of the mechanical treatment of the soil and comes on very soon after the breaking up of the capillary tubes.

Besides investigating these qualitative effects characteristic of the natural drying of the soil, an attempt was made to approach the question from the quantitative side by determining the thickness of the layer which assumes the necessary degree of dryness.   For this purpose special three-grained augers with one movable side were used.   Each auger was inserted into the soil until it penetrated the moist soil sufficiently deep; then it was removed together with the soil; the movable side being opened, the exposed inside of the auger showed the profile of the soil with the border line between dry and moist parts; the moisture content of these parts was determined.

The determinations were made on April 24, three weeks after the field work has been started.   The results are shown in table 20.

In this way, after 3 weeks of the vegetation period, the surface layer of the soil, averaging 4 cm. deep (one-third of the ordinary plowed layer), assumes the moisture content at which the increase in fertility of the soil due to drying becomes possible.

Then an attempt was made to compare the fertility of the naturally dried lumps produced in the field with the fertility of the surrounding moist soil. From the surface of the plot some of the dry lumps were collected at the time the surrounding moist soil was taken.   Both of the soil samples were made up to the same moisture content, packed into pots and sown with millet.

The soil samples were taken at three different periods:

1. On April 7 a soil sample was taken from an April fallowed plot, plowed on April 5 to the depth of 4 vershoks and harrowed on April 6.

The moisture content of the dry soil was 8.5 per cent, and of the moist soil 33.6 per cent.   Soon after the appearance of the millet seedlings it became evident that the better growth was in the pots with dry soil.   The difference increased steadily, reaching its culmination during the stage of heading out. During the subsequent growth period the differences began to disappear and the yields were the same according to the total weight, with only a slight increase in grain on the dried soil.

2. On April 27 samples were taken from a plot of an early autumn fallow, plowed in the autumn on August 20 to the depth of 4 vershoks and harrowed on April 5.   The only rain from the beginning of the spring was on April 13

TABLE 19

Moisture content* of various lumps of soil under natural conditions

PLACE OF SAMPLING	DATE OF SAMPLING	KIND OF SAMPLE	MOISTURE CONTENT OF TOTAL DRY SUBSTANCE	REMARKS
			per cent	
Fallow first working in April	April 6	Dry lumps / Moist lumps	11.00 / 32.19	The field was ploughed 4 vershkos deep on April 5; harrowed April 6, sampling was done several hours on a day after that; clear sunny day.
	April 7	Dry lumps / Moist lumps	8.55 / 34.77	
Fallow first working in April	April 18	Dry lumps / Dry large lumps / Moist soil	3.72 / 4.56 / 30.19	Samples from the same field after 12 days; the surface of the field is covered with a layer of large lumps, under which is the moist soil.
Field in potatoes the previous year	April 18	Dry surface crust / Moist layer beneath surface crust larger / Moist layer somewhat deeper	4.35 / 18.77 / 24.38	The field was not plowed in the fall; in the spring it was flooded; from the surface was separated out a thin crust, under which were the moist layers.
Early fall fallow	April 18	Dry lumps / Moist soil	4.11 / 31.53	The field was plowed in the fall, in August; and was harrowed in the spring.
Oat field	April 18	Dry lumps / Moist soil	3.74 / 35.56	The field was plowed in the spring, harrowed and sowed with oats; at sampling the oats were coming up.
First working of a clover field	April 18	Dry lumps / Moist soil	5.51 / 38.37	A day before the clover was plowed under.

Early fall fallow	June 9	Dry lumps	4.1	From the plot under the same name from which a sample was taken on April 18; during the period several inches of rainfall came down.
		Moist soil	18.68	
Early fall fallow	June 18	Dry lumps	3.47	Same as above with more rain in the meantime.
		Moist soil	15.05	
Early fall fallow	June 22	Dry lumps	2.44	Same as above with more rain.
		Moist soil	25.82	

*The averages of duplicate determinations are given.

to the depth of 0.2 mm. The plot was covered with a layer of dry soil 1½ cm. thick from which the dry samples were taken. The moist soil lying immediately underneath was taken to the same depth. The moisture content of the dry soil was 7.7 per cent, of the moist—30.28 per cent. The increase in growth on the dry soil was evident from the very beginning of the vegetative period, and gradually increased until the end of the growth period. As a result, the total yield and the size of the grain were much larger on the dry soil.

3. The third sample was taken from the same plot on June 23. Since the preceding sampling the field had been subjected once to harrowing. The drought which existed during April changed into a period of rainy weather

TABLE 20

Moisture content of various layers and depth of latter

PLACE OF SAMPLING	KIND OF SAMPLE	MOISTURE CONTENT OF TOTAL DRY SUBSTANCE	DEPTH OF THE DRY LAYER	REMARKS
		per cent	*cm.*	
April fallowing	Dry	12.40	3.0	The field was plowed to a depth of four vershoks on April 5 and harrowed on April 6
	Moist	25.44		
Early autumn fallowing	Dry	8.99	3.5	The field was plowed in the fall, August 20, to a depth of 4 vershoks and harrowed in the spring
	Moist	31.55		
Late autumn fallowing	Dry	7.03	4.0	The field was plowed in the fall, October 1, to a depth of four vershoks and harrowed in the spring
	Moist	31.70		
Oat field	Dry	8.23	4.0	Plowed and harrowed in the spring and sown to oats April 10
	Moist	29.40		
Oat field	Dry	7.20	1.5	Plowed to a depth of four vershoks in the fall, harrowed in the spring and sown to oats on April 12
	Moist	42.03		

from May 10 to 24, the total rainfall being 104 mm. A comparatively dry period followed from May 25 to June 9 (only 10.8 mm. rainfall), then 4 days with a large precipitation (27.8 mm.), and again a dry period until the time of sampling. The dry layer at the time of sampling was ⅜ vershok, and the moist soil was taken right underneath. The moisture content of the dry soil was 3.67 per cent, and of the moist, 25.32 per cent. In the first stage of vegetation a marked superiority of the pots with the dry soil over the pots with the moist soil was observed. Later on it began to disappear and yield-data showed the superiority of the dry soil in the total weight of the plants only. The yield data of all the three experiments are given in table 21.

In all three cases a measure was thus obtained by pot experiments of the change in soil fertility under the influence of natural drying of the soil surface

TABLE 21

Relative yields on dry and moist samples of soils

PLACE OF SAMPLING	DATE OF SAMPLING	CONDITION OF THE SOIL	MOISTURE CONTENT AT THE TIME OF TAKING	RELATION BETWEEN DRY- AND MOIST-SOIL YIELDS		
				Total weight	Grain	Straw
			per cent			
April fallowing..................	April 7	Moist	33.6	100	100	100
		Dry	8.5	100	113	88
Early autumn fallowing..........	April 24	Moist	30.28	100	100	100
		Dry	7.7	196	197	176
Early autumn fallowing..........	June	Moist	25.32	100	100	100
		Dry	3.67	121	94	142

TABLE 22

Relative yields on dried and moist plots in field experiments

YEAR	PLANT	SOIL	PLOT	RELATIONSHIP BETWEEN YIELDS ON MOIST AND DRIED SOILS		
				Total weight	Grain	Straw
1916	Millet	Unfertilized	Moist	100	100	100
			Dried	129	116	131
	Buckwheat	Unfertilized	Moist	100	100	100
			Dried	114	111	116
1917	Oats	Unfertilized	Moist	100	100	100
			Dried	116	134	108
		Manured	Moist	100	100	100
			Dried	123	120	126
	Millet	Unfertilized	Moist	100	100	100
			Dried	105	112	99
		Manured	Moist	100	100	100
			Dried	113	109	116
		Uncultivated	Moist	100	100	100
			Dried	119	121	117

layer during the vegetative period. The change in fertility was expressed by different degrees of intensity, sometimes increasing the growth only in its early stages, but sometimes bringing about a large increase in the yield of grain

and straw.   The differences observed may be attributed to many causes, for example, the leaching out by the rain of the compounds formed in the dried soil layer.

Finally an attempt was made to carry out an actual field experiment of drying.   With that purpose plots of 1 by 4 meters were staked out in the field and the plowed layer to the depth of 3 vershoks was removed and dried on iron sheets in the field.   After the drying the soil was made up to its original moisture content and replaced.   On the control plot the same removal and replacing of the plowed layer was carried out.   It was possible to bring the dried soil to a moisture content of 6 to 7 per cent; that of the moist soil was most of the time about 30 per cent.   The plots were then sown with different plants and the yields observed.   The results of the outlined experiments are given in table 22.

These results show that *the increase in fertility of the soil under the influence of drying may be obtained not only with plants grown under artificial conditions (pot experiments), but also under natural conditions in the field.*   Besides, just as in pot experiments, the uncultivated manured soil responds more strongly to drying than the unfertilized soil.   The magnitude of the increase in yield in the described field experiments expressed itself in smaller figures than in most of the pot experiments.   This phenomenon may be explained by the fact that in the field experiments, the natural drying of the soil during the period of growth, which took place on the dried soils as well as on the moist plots, could not be excluded; consequently the results of the experiment showed the difference in intensity of drying in both cases.

Summarizing the data in relation to the applicability of the raising of soil fertility by means of drying under natural conditions, the following may be said: (*a*) that the surface layers of the soil through the natural processes of drying are able to obtain the necessary moisture content to raise its fertility; (*b*) that according to pot experiments the soils dried in such a manner appeared to be more fertile than those that remained moist; and (*c*) that according to field experiments the naturally dried surface layer of the field plots increases its fertility.

From this we may draw, with a large degree of certainty, the final conclusion, *that the process of drying is a powerful factor determining to a large extent the fertility of the soil under natural conditions.*   It is probably playing an important, until now unknown, rôle in all the processes of increasing the soil fertility obtained by means of mechanical cultivation of soil.

<center>VIII</center>

Let us pass now to a more detailed consideration of this conclusion.   It has always been considered that the plowed layer of the soil is the place where the plants obtain their nutrients.   Although the roots of the plants spread out to a considerable depth, most of them are located here.   It is this layer that is manured; in it primarily go on the processes of fermentation which produce

the available nitrogenous substances; in it also takes place the decomposition of humus, on which depends the whole life activity of the soil and as a result, the nutrition of the plants. This surface layer, therefore, is the mysterious laboratory in which are created the main conditions of high or low yield. Large moisture content creating favorable conditions for the activity of the microorganisms, and good aeration guaranteeing a sufficient supply of oxygen, are considered as the main conditions determining the cultural condition of the soil. Based on these, it was natural to suppose that the maximum fertility of the soil surface layer is located at a little distance below its surface; there the required moisture, lacking in the upper layers, is found together with an abundant supply of oxygen which is lacking in the lower layers. *The center of fertility, therefore, has been thought to be a layer at a certain depth above or below which the fertility of the soil decreases; the very upper dried-out layer is only a necessary evil, for while this dry layer is inert from the standpoint of accumulation of fertility, it protects the layer beneath from drying out. This is the picture one gets, basing his conclusions on the predominating views on soil fertility.*

If the previously described supposition of drying the soil in connection with the natural formation of its fertility is correct, it is evident that the above picture of the distribution of the fertility must be changed. Aside from the important accumulation of the fertility through the activities of the microorganisms, we also have increases in fertility of the surface layer due to the drying, which is contrary to widespread opinion that the fertility of this layer remains unchanged.

With sufficient importance ascribed to drying as a cause of increased fertility, one must find the maximum fertility in the upper layer and a gradual fall in the lower ones. In 1920 this problem was approached in the following way:

A plot 2 by 2 meters was laid out on a fallowed field. The surface layer to the depth of 20 cm. was removed from the whole plot, mixed well on iron sheets in order to remove all possible differences in fertility, and immediately replaced. The plot was left fallow; the only treatment it received was weeding by hand, and keeping a mellow surface by means of an iron rake. In order to protect the plot from rain special glass frames were placed one arshin[10] above the surface, insuring the proper ventilation, at night and on rainy days. Also, to avoid too great a drying the soil was watered with a watering can three times (May 3, 10, and 15) the amount of water each time corresponding to 7 mm. of precipitation. Samples of soil were taken from that plot every two weeks, in layers 0 to 5, 5 to 10, 10 to 15, 15 to 20, 20 to 30, 30 to 40, and 40 to 50 cm. A trench 50 cm. wide, the walls of which were reinforced with boards and covered with planks in order to diminish evaporation, was made along one of the sides of the plot for the purpose of sampling. Each sample of soil was sifted and packed into pots, with all the usual precautions to insure equalization of the moisture content of the different layers. Care was taken to prevent

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[10] One arshin equals 28 inches.

drying during the determination of the moisture content of the samples. The pots were sown with millet.

Five series of pots were prepared from which it was possible to establish the relations of separate soil layers within each series. The absolute yields of separate series could not, of course, be compared, since they were set up at different times, but by changing them into relative figures it was possible to obtain a definite picture of the changes in fertility in individual layers in relation to each other within each series. Since the yield from the 40 to 50-cm. layer could be considered as constant during the whole experiment, by taking it as a unit it was possible to compare the series.

One may see that the fertility of each of the overlying layers increases as compared with the lower layer. Since the supposition that the fertility of the lower layer during fallowing decreases for some reason seems to be improbable,

TABLE 23

The yield of separate layers of soil in the different series as compared with the yield of the layer 40 to 50 cm., taken as a unit

DEPTH	APRIL 15	MAY 3	MAY 15	MAY 31	JUNE 12
cm.					
0–5	4.5	7.2	10.5	14.4	20.3
5–10	4.5	6.0	7.5	11.7	15.5
10–15	4.5	4.8	6.8	9.6	13.8
15–20	4.5	4.6	6.3	8.4	10.3
20–30	1.5	2.0	4.0	2.4	2.8
30–40	1.2	0.8	1.6	1.4	1.8
40–50	1.0	1.0	1.0	1.0	1.0

and since it seems more possible to assume the opposite, one must conclude *that the fertility of all the soil layers increases during the vegetative period.* The increase during these two months of fallowing reaches about three times the original condition of the soil. The first four horizons, as would be expected, are the most fertile; these layers embrace 0 to 20 cm. and represent the surface layer of the soil. The subsoil layers appeared to be markedly less fertile. The increase in soil fertility of the different layers is also unequal and for the 2 months of fallowing can be expressed in the following figures:

THE LAYER	THE INCREASE IN FERTILITY
cm.	
0–5	4.5 times
5–10	3.3 times
10–15	3.0 times
15–20	2.3 times
20–30	1.9 times
30–40	1.5 times
40–50	1.0 times

The upper horizon appears to be not only the most fertile one, but is also marked by the greatest increase in fertility, as compared with all other layers; this supports the assumption that the condition of its fertility is largely determined by the phenomena of its drying."   An attempt was then made to determine what takes place in the surface layer when it is turned under, the phenomenon being analogous to the plowed layer.   For this purpose on one part of the above mentioned plot the surface soil was removed and immediately replaced but in the reverse order, that is to say, the layer 0 to 5 cm. was placed below and the layer 15 to 20 cm. above.   The soil samples from the turned-over portion of the plot were taken together with those from the normal portion of the plot; they were packed into pots of the same size and were sown with millet on the same day.   In such a way it was possible to compare both results completely.   Taking as before the yield of the layer 40 to 50 cm. as a unit, the data in table 24 was obtained.

TABLE 24

Relative yield of separate layers of soil when placed in reverse order

DEPTH OF LAYER	MAY 15		MAY 31		JUNE 12	
	Unturned	Turned	Unturned	Turned	Unturned	Turned
cm.						
0–5	10.5	6.3	14.4	8.2	20.3	23.1
5–10	7.5	6.8	11.7	12.1	15.5	22.2
10–15	6.8	7.5	9.6	12.7	13.8	15.6
15–20	6.3	10.5	8.4	6.3	10.3	9.6
20–30		4.0		2.4		2.8
30–40		1.6		1.4		1.8
40–50		1.0		1.0		1.0

In the turned-over surface layer, after 2 weeks one could note that the fertility of the exposed lower horizon increased; the fertility of the upper horizon plowed under decreased.   After 2 more weeks the normal picture of the distribution of the fertility was established, expressed by a maximum fertility in the upper layer with a consequent diminution as the layer went deeper.

In such a way with artificial dislocation of horizons of the surface layer its fertility changes very abruptly and then *begins to return to its normal distribution which appears to be a maximum in the upper layer with consequent diminution lower down.*

[11] We deem it necessary to emphasize that both of the above described experiments on the distribution of soil fertility, are not to be considered as final proof in support of the exclusive effect of the phenomenon of drying of soil on the building of its fertility.   These facts assist only in establishing more firmly the hypothesis; moreover, the only other possible explanation of the described phenomena may be the accumulation of nutritive compounds in the upper layers by means of the current of evaporating water.   According to the material on hand which will be the subject of a later communication, this has a very limited influence.

CONCLUSIONS

From what has been presented in this paper it may be assumed that there is ground for a serious consideration of the question of the rôle of drying soils. Especially is this important if one is to appreciate the methods for raising the soil fertility by means of mechanical treatment, or even for an appreciation of the systems of cropping. Is it not possible to look upon the methods of inter-tillage from this standpoint, instead of the accepted ideas of conserving moisture and increasing the aeration? May not the same question be raised in connection with the method of ridging potatoes? Is it not necessary to give a different interpretation to that system of intensive agriculture which includes special methods for drying the surface layers for the purpose of killing weeds and the conservation of moisture? Is not the drying of soil a key to a deeper appreciation of the system of sod or grass rotations, in which the soil on account of continuous tillage ceases to respond to mechanical treatment, but which attains its properties of raising the fertility under the influence of drying?

FUNDAMENTAL PRINCIPLES

1. The drying of the soil to an air-dried condition in the open air at ordinary temperatures produces a large increase in the yielding capacity in the case of pot experiments.

2. The degree of increase in yielding capacity depends on the preceding cultural conditions of the soil. Especially responsive to drying appear to be the uncultivated soils, and those occupied by many years of grass culture; soils under continuous mechanical treatment respond less readily. Soils fertilized with stable manure or phosphates are more responsive than unfertilized soils. All other conditions being equal, the response of a soil to drying increases as the fertility decreases.

3. Different plants react differently to the drying of the soil. The greatest increase in yielding capacity is shown by meadow grasses, then come the field legumes, then the field grasses, and lastly the intertilled plants.

4. A positive influence of drying is evident only with cultivated soils reaching a 6 per cent moisture content, and with uncultivated soils reaching 14 per cent. With smaller degrees of drying not only no increase in fertility is observed but in most cases it is lowered.

5. Repeated drying of one and the same sample of soil with intermediate moistenings is accompanied by a further increase in the yielding capacity, and the maximum fertility is attained with triple drying.

6. The maximum effect of drying for deep black soil seems to be in the layers 20 to 40 and 40 to 60 cm. For surface soils (0 to 20 cm.) as well as for the layer lower than 60 cm., it is markedly less.

7. During the process of drying, important chemical changes take place in the soil, expressing themselves in a large increase in the solubility of organic substances, a large enrichment of the soil samples with nitrogen and phosphorous,

an extremely large increase in the soil of the ammonia nitrogen, a considerable increase of amide nitrogen and a sharp diminution in microörganisms.

8. All these changes are very similar to those taking place in the soil under the influence of low temperatures and antiseptics, as a consequence of which the drying of a soil may be considered as its partial sterilization.

9. Out of the four factors acting on the soil during its drying (removal of water through evaporation, increased influence of the oxygen, heating by sun rays and the effect of the light as such) the increase in fertility is dependent upon dehydration and temperature. Oxygen and light, on the contrary, cause a decrease in fertility.

10. The soil under natural conditions, with the aid of ordinary methods of mechanical cultivation, in the upper layer easily attains the moisture content necessary for the positive effect on fertility.

11. The soil which has naturally dried out in the field, according to pot experiments appears to be much more fertile than the dried soil lying nearby.

12. Artificial drying of the surface layer carried out in the field on several plots produced an increased growth of the plants grown on them.

13. The sum total of the above considerations leads to the conclusion that the process of drying is a factor controlling to a large extent the fertility of the soil, and as such must play an important rôle (until now unknown) in all processes of increasing the soil fertility, which is being achieved by the methods of mechanical cultivation of the soil.

14. As an indirect proof of this, the distribution of fertility in the surface soil and its changes during the vegetative period showed that the upper 5-cm. layer is the most fertile and also increases its fertility most rapidly; lower down the fertility of the soil decreases and the rate of increase during the vegetative period diminishes.

<div align="center">REFERENCES</div>

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ALKALI STUDIES: I. TOLERANCE OF WHEAT FOR ALKALI IN IDAHO SOIL[1]

RAY E. NEIDIG and H. P. MAGNUSON

In connection with extensive investigations dealing with the reclamation and prevention of alkali lands in Idaho, it was found advisable to conduct tolerance studies for various crops grown under Idaho soil and climatic conditions. This paper concerns the crop of wheat and is the first of a series reporting the data secured on these studies. Additional papers dealing with other crops will follow.

The necessity for tolerance studies of crops in various alkali regions is manifest, since tolerance of a crop for alkali depends upon many factors such as type of soil, type of salts and concentrations of the soil solution, and the location of the salts in the soil at various periods of the plant's growth. All such factors vary so greatly that the subject indeed becomes very complex.

It is patent from results in former alkali investigations reported in the literature that to establish definitely the effect of alkali concentrations on plant growth, two factors must be carefully considered; first, these studies should include not only added salt concentrations, but more important, the determination of the recoverable salt concentration in a soil. Headley, Curtis and Scofield (2) have clearly shown that the true measure of the effect of alkali salts on crop growth is determined by the amount of recoverable salts in the soil solution rather than the amount added. Secondly, tolerance studies, to be of greatest benefit, must be carried on during the entire growth cycle of the crop before definite and satisfactory conclusions can be drawn. These tolerance studies become more valuable when conducted on a sufficient amount of soil so that several crops can be grown on the same soil and data secured on the concentration of alkali salt recoverable from the soil after each crop. It is well known by investigators in alkali soil problems, that plants may germinate freely, grow for a short period, and then die because of alkali concentrations. The true criterion of tolerance of a crop for alkali is the capacity of a plant to grow to maturity and produce a crop, not merely the capacity to germinate and grow for a short period and die. That such conclusions are true will be shown when the data on all tolerance studies are presented.

A preliminary field alkali survey was conducted in Idaho with a view to ascertaining the predominating alkalies present in the soil. These results

will appear in published form at a later date.   The predominating salts found in the soils analyzed were sodium carbonate, sodium chloride, and sodium sulphate, these salts occurring sometimes alone, but usually in various combinations.   Our tolerance experiments, therefore, were conducted with these salts, and a characteristic soil was prepared to which these salts were added in definite concentrations both alone and in combinations, in order that exact information on the tolerance of crops would be obtained.

DETAILS OF THE EXPERIMENT

For the tolerance studies a car load of surface soil was secured from a comparatively alkali-free area on the Caldwell Substation Farm and shipped to Moscow.   This soil is the bulk sample used in all the alkali concentrations in the tolerance studies.   The soil is listed in the United States Soil Survey (3) as Boise Silt Loam Soil and is a characteristic soil for a large area.   The mechanical analysis and moisture equivalent are given in table 1.

TABLE 1

Mechanical analysis and moisture equivalent of soil used

	PER CENT
Clay	8.56
Silt	46.00
Very fine sand	22.31
Fine sand	18.65
Medium sand	1.30
Coarse sand	1.86
Fine gravel	0.93
Moisture equivalent.........................21.2	

The entire car load was freed from lumps, thoroughly mixed, air dried and stored in a bin.   Before making up each alkali series, a moisture determination was made on the soil in order that the concentrations of added alkali could be made upon the basis of the moisture-free soil.

In all tolerance studies, the method of preparing the soil and general details of manipulation are similar, hence a complete description will be given in this first publication.   The alkali salts used were chemically pure anhydrous sodium carbonate, sodium chloride and sodium sulphate.

PREPARATION OF THE ARTIFICIAL ALKALI SOILS

The method of mixing the alkali salts and soil consisted of weighing out sufficient soil to equal the desired moisture-free amount required and transferring to a rotary concrete mixer.   To this soil was added the required amount of the alkali salts.   The mixing was continued until a complete and uniform

soil-alkali-mixture was obtained. Two 4-gallon jars were filled with a weighed quantity of soil. In addition a 2-gallon jar was filled from the same mix. Crops were grown on the 4-gallon jars, and the 2-gallon jar of soil served as a non-cropped check. All of the salt-soil concentrations were prepared in this manner.

After the entire series of pots was prepared, distilled water was added to each jar in amounts sufficient to bring the moisture content to approximately 20 per cent. After the soil had stood long enough to insure a uniform moisture condition, samples were taken from the duplicate jars for analysis in the following manner: two cores of soil were taken from each duplicate jar by means of a brass tube 1½ inches in diameter and sufficiently long to take a soil core through the entire depth of the jar. An analysis was made on a composite sample of the four cores. The results were taken as the average salt content of the duplicate jars. After the growth of each crop a composite sample of three cores was taken from each of the duplicate jars, and analyzed. All percentages are calculated on the basis of anhydrous soil.

The method of analyzing the soil for alkali salts in use in this laboratory has already been described in a former publication (4) and will not be repeated here.

EXPERIMENTAL WORK

Eighty-four 4-gallon jars were filled with equal amounts of soil to which various alkali concentrations and combinations were added. The series represents 40 different treatments in duplicate, and also 4 check jars of soil which received no alkali applications. The series of jars were placed in the greenhouse and enough distilled water added to increase the moisture content of the soil to 15 or 20 per cent. After standing a few days to insure a uniform soil moisture, the soils were sampled and alkali salts determined. The sample holes were then filled in and 15 kernels of Blue Stem wheat were planted in each duplicate jar. The soils were kept at an approximate moisture content of 18 per cent during the growing period. Data were taken at frequent intervals on germination, rate of growth, time of heading out, total yield of crops and the general appearance of the plants in all treatments. The number of plants in each jar was reduced to 8 when their height reached approximately 15 inches. At the time of maturity, the crop was harvested, dried and weighed. The grain was threshed and weighed separately. Samples of soil were taken from each jar and analyzed for the alkali salt content.

After the removal of the first crop and when the soil was sampled, it was turned out of each jar, thoroughly mixed and returned to the jar, moistened and another crop of wheat planted. This second crop was grown and records were taken in the same manner as for the first.

Table 2 contains data showing the concentrations of alkali salts added to the prepared soils; the initial recoverable alkali concentrations together with the recoverable alkali after removing the first and second crops. Table 3 shows the percentage of germination of the wheat, and the yield for each crop.

TABLE 2
Average of salts recovered from duplicate pots

POT NUMBER	TREATMENTS			INITIAL SAMPLING				FIRST CROP				SECOND CROP			
	$NaCO_3$	NaCl	Na_2SO_4	$NaCO_3$	NaCl	Na_2SO_4	Total	$NaCO_3$	NaCl	Na_2SO_4	Total	$NaCO_3$	NaCl	Na_2SO_4	Total
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
141	Check			0.034	0.000	0.020	0.054	0.026	0.000	0.005	0.031	0.034	0.000	0.011	0.046
79	0.20			0.096	0.000	0.005	0.101	0.088	0.000	0.006	0.094	0.097	0.000	0.014	0.111
81	0.40			0.171	0.000	0.007	0.178	0.134	0.000	0.006	0.141	0.160	0.000	0.008	0.169
83	0.60			0.231	0.000	0.006	0.237	0.190	0.000	0.005	0.195	0.204	0.000	0.006	0.210
85	0.90			0.383	0.000	0.009	0.392	0.312	0.000	0.005	0.317	0.310	0.000	0.011	0.321
87		0.10		0.036	0.067	0.008	0.111	0.027	0.095	0.000	0.123	0.033	0.046	0.002	0.081
89		0.20		0.036	0.134	0.007	0.177	0.026	0.182	0.006	0.214	0.053	0.072	0.005	0.131
91		0.40		0.036	0.254	0.006	0.296	0.023	0.257	0.001	0.281	0.051	0.064	0.003	0.118
93			0.20	0.031	0.000	0.143	0.174	0.023	0.001	0.185	0.209	0.036	0.000	0.197	0.233
95			0.40	0.031	0.000	0.306	0.337	0.027	0.000	0.395	0.422	0.033	0.003	0.348	0.384
97			0.60	0.036	0.000	0.481	0.517	0.025	0.000	0.537	0.563	0.035	0.000	0.464	0.499
99			0.90	0.029	0.000	0.697	0.726	0.024	0.001	0.755	0.780	0.035	0.000	0.652	0.687
101	0.10	0.10		0.049	0.092	0.013	0.154	0.047	0.071	0.010	0.128	0.057	0.032	0.010	0.100
103	0.30	0.05		0.128	0.052	0.007	0.187	0.127	0.028	0.009	0.164	0.115	0.018	0.012	0.146
105	0.10	0.30		0.053	0.268	0.006	0.327	0.042	0.208	0.005	0.256	0.052	0.091	0.003	0.147
107	0.60	0.10		0.227	0.100	0.000	0.327	0.201	0.078	0.012	0.292	0.207	0.036	0.008	0.252
109	0.20	0.20		0.086	0.118	0.007	0.211	0.078	0.102	0.003	0.184	0.095	0.051	0.004	0.150
111		0.05	0.20	0.031	0.046	0.191	0.268	0.019	0.044	0.159	0.222	0.038	0.025	0.126	0.190
113		0.30	0.10	0.034	0.234	0.124	0.392	0.021	0.240	0.065	0.326	0.043	0.116	0.062	0.221
121		0.10	0.40	0.029	0.062	0.302	0.393	0.020	0.071	0.313	0.405	0.037	0.057	0.309	0.404
123		0.10	0.60	0.026	0.079	0.526	0.631	0.020	0.109	0.397	0.527	0.019	0.058	0.476	0.554
125	0.10		0.10	0.057	0.000	0.091	0.148	0.052	0.000	0.120	0.172	0.056	0.000	0.074	0.130
127	0.20		0.20	0.086	0.000	0.157	0.243	0.096	0.000	0.138	0.234	0.080	0.000	0.148	0.228
129	0.30		0.40	0.129	0.000	0.332	0.461	0.124	0.000	0.175	0.299	0.183	0.002	0.153	0.338
131	0.20		0.60	0.084	0.000	0.471	0.555	0.082	0.000	0.488	0.570	0.077	0.000	0.478	0.555

133	0.60		0.10	0.242	0.000	0.082	0.324	0.216	0.000	0	0.279	0.219	0.0	0.047	0.269
135	1.00	0.05	0.10	0.379	0.000	0.066	0.445	0.328	0.002	0	0.426	0.340	0.0	0.064	0.412
137	0.05	0.10	0.05	0.039	0.053	0.076	0.168	0.040	0.016	0.028	0.084	0.048	0.0.5	0.025	0.088
139	0.10	0.10	0.10	0.056	0.073	0.163	0.292	0.049	0.080	0.099	0.228	0.066	0.0.8	0.062	0.166
143	0.20	0.05	0.10	0.095	0.091	0.122	0.308	0.099	0.056	0.071	0.226	0.102	0.0.3	0.087	0.232
145	0.40	0.10	0.10	0.178	0.061	0.116	0.355	0.186	0.045	0.099	0.331	0.169	0.019	0.048	0.236
147	0.60	0.10	0.20	0.245	0.098	0.189	0.532	0.223	0.089	0.188	0.500	0.202	0.078	0.176	0.475
24	0.40	0.10	0.40	0.147	0.096	0.386	0.629	0.152	0.080	0.287	0.520	0.138	0.043	0.219	0.401
26	0.20	0.05	0.40	0.079	0.034	0.442	0.555	0.058	0.043	0.628	0.790	0.086	0.027	0.355	0.468
2	0.20	0.05	0.80	0.080	0.035	0.875	0.990	0.036	0.053	0.660	0.750	0.062	0.023	0.590	0.676
4	0.05	0.05	0.60	0.034	0.037	0.724	0.795	0.073	0.066	0.396	0.535	0.040	0.027	0.515	0.583
12	0.10	0.05	0.10	0.057	0.040	0.200	0.297	0.057	0.036	0.081	0.175	0.055	0.036	0.095	0.187
18	0.40	0.10	0.60	0.094	0.065	0.453	0.612	0.106	0.110	0.457	0.673	0.096	0.083	0.551	0.731
31	0.30	0.20	0.20	0.100	0.138	0.179	0.417	0.085	0.175	0.172	0.432	0.109	0.183	0.217	0.509
34	0.10	0.20	0.20	0.053	0.106	0.199	0.358	0.042	0.183	0.143	0.368	0.043	0.126	0.178	0.347
75	0.10	0.40	0.10	0.047	0.271	0.086	0.404	0.043	0.253	0.057	0.354	0.049	0.146	0.068	0.264
				0.037	0.000	0.003	0.040	0.036	0.000	0.004	0.041	0.036	0.000	0.006	0.041

Tables 4, 5, 6 and 7 are made up of averages for duplicate pots similarly compiled to show the particular combinations under discussion. Table 8

TABLE 3

Averages of percentage germination and of crop yields, regarding the check as 100 per cent

POT NUMBER	TREATMENTS			GERMINATION		YIELD		
	Na_2CO_3	NaCl	Na_2SO_4	First crop	Second crop	First crop	Second crop	Total
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
141	Check			96	96	100.0	100.0	100.0
79	0.20			86	86	70.7	121.0	94.3
81	0.40			70	87	90.9	192.8	120.6
83	0.60			86	67	59.6	31.4	41.1
85	0.90			50	70	0.0	0.0	0.0
87		0.10		90	93	108.2	87.0	102.0
89		0.20		80	93	103.0	101.0	102.7
91		0.40		63	90	79.4	139.2	96.7
93			0.20	93	93	101.6	95.1	99.8
95			0.40	90	90	106.3	142.8	117.0
97			0.60	96	86	112.7	119.6	114.9
99			0.90	90	96	91.1	162.5	111.3
101	0.10	0.10		70	90	95.4	124.8	104.1
103	0.30	0.05		93	100	97.3	150.9	113.1
105	0.10	0.30		86	93	64.0	185.3	99.7
107	0.60	0.10		80	87	56.5	215.1	103.0
109	0.20	0.20		90	86	97.3	173.8	118.6
111		0.05	0.20	86	90	98.0	113.1	101.7
113		0.30	0.10	90	90	72.1	189.6	106.8
121		0.10	0.40	73	96	60.5	180.9	95.8
123		0.10	0.60	93	100	50.4	233.2	107.5
125	0.10		0.10	80	66	98.2	107.6	98.6
127	0.20		0.20	90	100	99.4	143.3	112.2
129	0.30		0.40	80	90	101.1	201.5	130.6
131	0.20		0.60	83	90	112.2	161.3	126.5
133	0.60		0.10	76	90	64.2	147.2	96.7
135	1.00		0.10	43	77	0.0	0.0	0.0
137	0.05	0.05	0.05	86	86	105.9	132.1	113.7
139	0.10	0.10	0.10	83	96	107.8	109.1	107.1
143	0.20	0.10	0.10	86	86	113.8	140.6	121.6
145	0.40	0.05	0.10	90	90	124.5	151.0	132.5
147	0.60	· 0.10	0.20	76	76	29.5	108.7	52.6
24	0.40	0.10	0.40	80	90	73.9	187.2	207.2
26	0.20	0.05	0.40	93	86	103.8	216.3	139.7
2	0.20	0.05	0.80	76	70	46.0	182.2	85.9
4	0.05	0.05	0.60	87	96	98.1	201.5	128.4
12	0.10	0.05	0.10	96	86	90.5	123.2	102.3
18	0.40	0.10	0.60	90	90	58.6	156.0	87.3
31	0.30	0.20	0.20	96	83	56.7	146.4	83.0
34	0.10	0.20	0.20	86	100	59.8	176.5	94.1
75	0.10	0.40	0.10	56	83	18.0	161.1	59.3

contains the data for the fallow pots showing salt additions and recoveries corresponding to those shown in table 2.   The averages of duplicate pots have

TABLE 4

Salt combinations in which sodium carbonate predominates

NUMBER	CONCENTRATION OF ALKALI ADDED			CONCENTRATION OF ALKALI RECOVERED				CROP YIELD— FIRST CROP
	Na₂CO₃	NaCl	Na₂SO₄	Na₂CO₃	NaCl	Na₂SO₄	Total	
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
83	0.6			0.190	0.000	0.050	0.195	59.6
107	0.6	0.1		0.201	0.078	0.012	0.291	56.5
133	0.6	0.1		0.216	0.000	0.063	0.279	64.2
147	0.6	0.1	0.1	0.223	0.089	0.188	0.500	29.5

TABLE 5

Combinations showing a medium concentration of sodium carbonate

NUMBER	CONCENTRATION OF ALKALI ADDED			CONCENTRATION OF ALKALI RECOVERED				CROP YIELD— FIRST CROP
	Na₂CO₃	NaCl	NaSr₄O₄	Na₂CO₃	NaCl	Na₂SO₄	Total	
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
81	0.4			0.134	0.000	0.006	0.141	90.0
103	0.3	0.05		0.127	0.028	0.009	0.164	97.3
129	0.3		0.4	0.124	0.000	0.175	0.299	101.1
143	0.2	0.10	0.1	0.099	0.056	0.071	0.226	113.8
24	0.4	0.10	0.4	0.152	0.080	0.287	0.520	73.9
18	0.4	0.10	0.6	0.106	0.110	0.457	0.673	58.6
31	0.3	0.20	0.4	0.085	0.175	0.172	0.432	56.7
109	0.2	0.20		0.078	0.102	0.003	0.184	97.3

TABLE 6

Salt combinations in which sodium chloride predominates

NUMBER	CONCENTRATION OF ALKALI ADDED			CONCENTRATION OF ALKALI RECOVERED				CROP YIELD— FIRST CROP
	Na₂CO₃	NaCl	Na₂SO₄	Na₂CO₃	NaCl	Na₂SO₄	Total	
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
89		0.2		0.026	0.182	0.006	0.214	103.0
109	0.2	0.2		0.078	0.102	0.003	0.184	97.3
123		0.2	0.6	0.020	0.109	0.397	0.527	50.4
18	0.4	0.1	0.6	0.106	0.110	0.457	0.673	58.6
31	0.3	0.2	0.2	0.085	0.175	0.172	0.432	56.7
34	0.1	0.2	0.2	0.042	0.183	0.143	0.368	59.8
91		0.4		0.023	0.257	0.001	0.281	79.4
105	0.1	0.3		0.042	0.208	0.005	0.256	64.0
113		0.3	0.1	0.021	0.240	0.065	0.326	72.1
	0.4	0.4	0.1	0.043	0.253	0.057	0.354	18.0

been plotted in the graphs in figures 1, 2 and 3, showing the amount of salt applied, the average amount recovered at each determination and the average

of crop results expressed in percentage above or below the check. The average of the check pots is considered 100 per cent. The first number of the set of duplicate pots is used to represent the average in the graphs.

In the discussion of the tables that follows, the term maximum tolerance is used to express the concentration of a single salt at which a decrease in crop growth consistently appears. There is found a relatively wide range between this point and that at which a marked decrease in crop-growth results. This amount of recoverable salt is called the critical concentration. The terms are arbitrarily assigned to these rather well defined points in the toxicity range and used for convenience in discussing the data.

TABLE 7

Salt combinations in which sodium sulfate predominates

NUMBER	CONCENTRATION OF ALKALI ADDED			CONCENTRATION OF ALKALI RECOVERED				CROP YIELD—FIRST CROP
	Na₂CO₃	NaCl	Na₂SO₄	Na₂CO₃	NaCl	Na₂SO₄	Total	
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
97			0.6	0.025	0.000	0.537	0.563	112.7
99			0.9	0.024	0.001	0.755	0.780	91.1
123		0.10	0.6	0.020	0.109	0.397	0.527	50.4
131	0.20		0.6	0.082	0.000	0.488	0.570	112.2
2	0.20	0.05	0.8	0.036	0.053	0.660	0.750	46.0
4	0.05	0.05	0.6	0.073	0.066	0.396	0.535	98.0
18	0.40	0.10	0.6	0.106	0.110	0.457	0.673	58.6
95			0.4	0.027	0.000	0.395	0.422	106.3
121		0.10	0.4	0.020	0.071	0.313	0.405	60.5
129	0.30		0.4	0.124	0.000	0.175	0.299	101.1
24	0.40	0.10	0.4	0.152	0.080	0.287	0.520	73.9
26	0.20	0.05	0.4	0.058	0.043	0.688	0.790	103.8

In comparing the graph numbers 83, 107, 133, 147, the striking feature is the increased recovery of sodium carbonate salts when chlorides and sulphates are present either alone or in combination. Slightly more sodium carbonate is recovered when sodium sulfate is present than when sodium chloride is added. In the face of this recovery, the yield of crop is slightly higher in the sodium sulfate addition, which in turn shows a higher carbonate recovery. This indicates a lower toxicity for sodium sulfate than sodium chloride. When the concentrations 0.1 per cent sodium chloride and 0.1 per cent sodium sulfate are added to 0.6 per cent sodium carbonate, the sodium carbonate recovery is greatest. Here the total salt concentration is sufficient to reduce the yield 75 per cent. It must be remembered that 0.19 to 0.22 per cent recoverable sodium carbonate is very near the critical concentration. Very little additional salt is necessary at this concentration entirely to inhibit growth.

The series reported in table 5, gave recoveries of sodium carbonate within a close range, but varying recoveries of sodium chloride and sodium sulfate. The crop growth appeared to be inversely proportional to the recoveries of
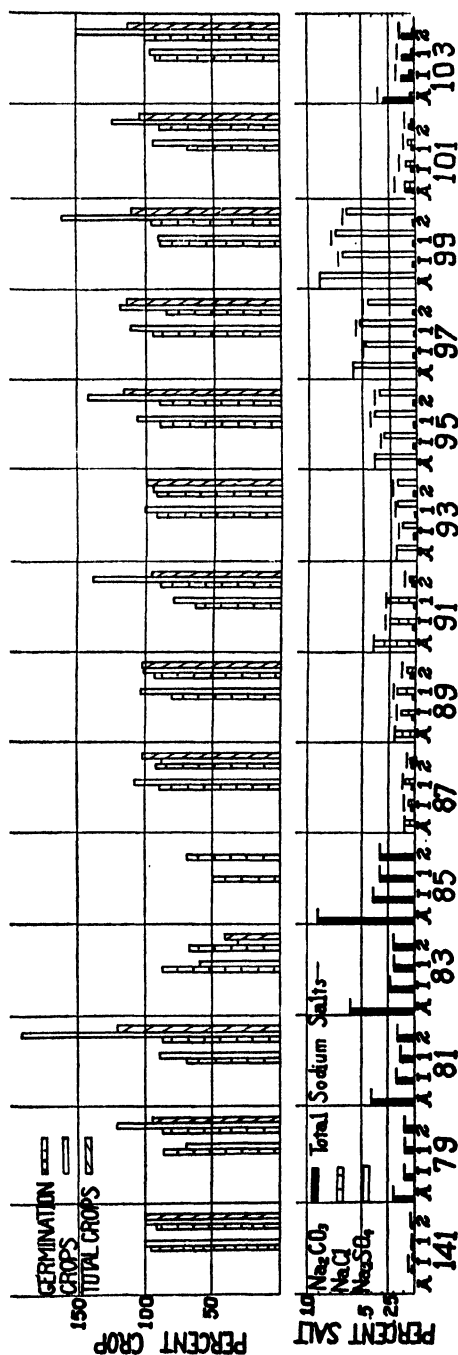
FIG. 1. GRAPHS OF AVERAGES OF DUPLICATE POTS, SHOWING ADDITIONS AND RECOVERIES OF EACH SALT AND OF TOTAL SODIUM SALTS, GERMINATION OF EACH CROP, PERCENTAGE YIELD OF EACH CROP, AND OF TOTAL OF THE TWO CROPS, USING THE AVERAGE OF THE CHECKS AS 100 PER CENT

A, salts added. I, salts recovered at initial sampling. 1, first crop and salts recovered when first crop is harvested. 2, second crop and final salt recovery.
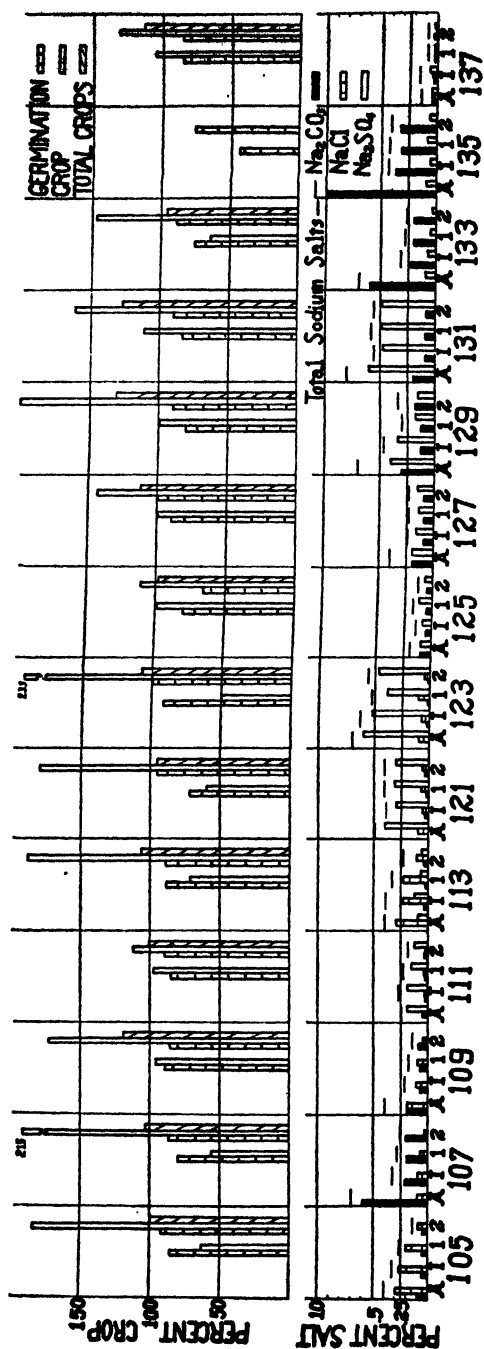
FIG. 2. GRAPHS OF AVERAGES OF DUPLICATE POTS, SHOWING ADDITIONS AND RECOVERIES OF EACH SALT AND OF TOTAL SODIUM SALTS, GERMINATION OF EACH CROP, PERCENTAGE YIELD OF EACH CROP, AND OF TOTAL OF THE TWO CROPS, USING THE AVERAGE OF THE CHECKS AS 100 PER CENT

A, salts added. I, salts recovered at initial sampling. 1, first crop and salts recovered when first crop was harvested. 2, second crop an final salt recovery.
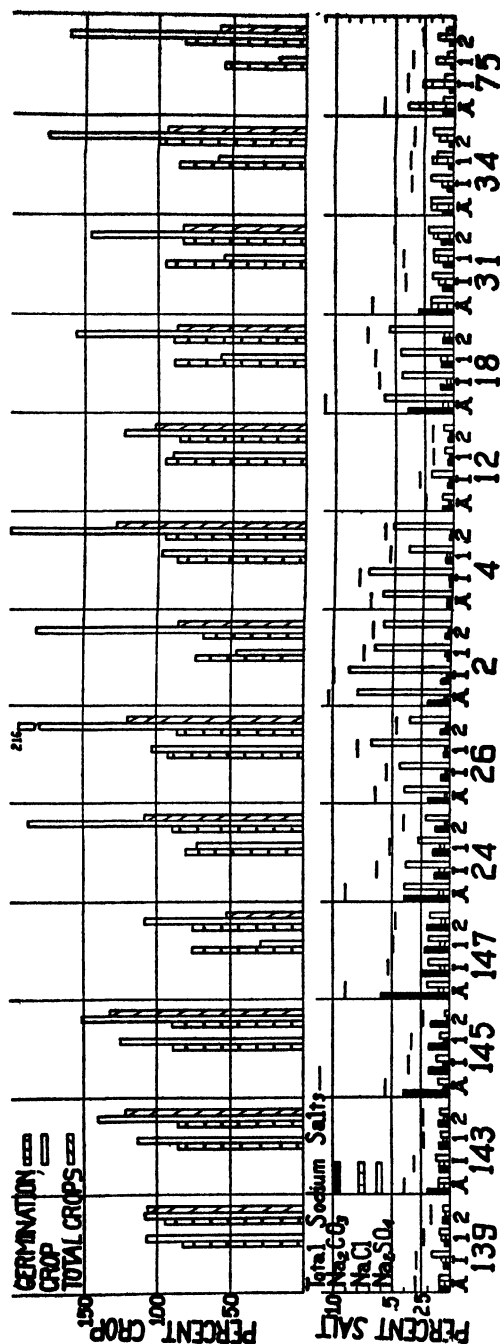
FIG. 3. GRAPHS OF AVERAGES OF DUPLICATE POTS, SHOWING ADDITIONS AND RECOVERIES OF EACH SALT AND OF TOTAL SODIUM SALTS, GERMINATION OF EACH CROP, PERCENTAGE YIELD OF EACH CROP, AND OF TOTAL OF THE TWO CROPS, USING THE AVERAGE OF THE CHECKS AS 100 PER CENT

A, salts added. I, salts recovered at initial sampling. 1, first crop and salts recovered when first crop was harvested. 2, second crop and final salt recovery.

sodium chloride, while the sodium carbonate recovery remained approximately a constant. Variations in recovery of sodium sulfate do not seem to affect yield greatly in the above combinations. Sodium chloride recovery is the chief factor. The effect of sodium sulfate recoveries is chiefly shown when the concentration of carbonate or chloride is near the critical point. A recovery of 0.1 per cent sodium carbonate in water extract of the soil closely approaches the maximum tolerance concentration for wheat. Any additional percentage recovery is shown in a decreased yield. At the above observed maximum tolerance concentration of sodium carbonate, variations in either sodium chloride or sodium sulfate recoveries will show an effect on crop yield. The former salt shows much greater toxicity than the latter.

Table 6 contains data showing the effect of sodium chloride on crop growth when it is present in the soil solution in an amount approximating maximum tolerance and the critical concentration for wheat growth. Both groups represent individual sodium chloride recoveries and recoveries of sodium chloride in combination with other alkali salts. For sodium chloride the maximum tolerance is between 0.18 and 0.25 per cent expressed as recoverable salt. In general it approximates 0.2 per cent expressed as recoverable salt. Any increase in percentage of recoverable sodium chloride, however slight, tends to approach rapidly the critical concentration for crop growth. Any slight increase in the percentage recoveries of the other two salts when in combination with the 0.2 per cent sodium chloride recovery rapidly changes the effect on crop growth from maximum tolerance to the critical concentration or sometimes entirely inhibits plant growth.

In the second part of the table where 0.25 per cent recoverable sodium chloride is observed, very slight increases of recoverable salts rapidly approach total inhibition of crop growth. This concentration (0.25 per cent) of sodium chloride is very near the limit of alkali tolerance for crop growth and will be influenced by the recovery of even very small amounts of other salts.

In comparing graphs 147 and 24 with very similar recoveries of sodium chloride, the effect of an increased recovery of sodium carbonate is very clearly shown by the reduced yield. The total salt recoveries in the combination showing the greater reduced yield, is slightly less than with the higher crop-yielding combination. This clearly shows the more toxic effect of sodium carbonate as compared with sodium sulfate. It also shows the added toxic effect of sodium chloride salts. These same combinations without sodium chloride were far less toxic to plant growth. Here is seen the added toxic effect of a small amount of sodium chloride when accompanying the other two salt concentrations, which in themselves do not show a marked toxic effect on wheat growth.

Table 7 contains data showing the effect on crop yield of sodium sulfate alone and in combination with other alkali salts. No appreciable effect on the growth of wheat of even the highest recoveries of sodium sulfate is noted. All concentrations of sodium sulfate used in this experiment were below the toxic limit for this salt.

High concentrations of sodium sulfate when accompanied by small recoveries of sodium chloride show a marked decrease in crop yield, due to the toxic effect of the sodium chloride. This is shown clearly in the graphic illustration of results of treatments numbers 97, 123 and 121. The addition of 0.6 per cent sodium sulfate shows a normal yield, while this amount accompanied by 0.1 per cent sodium chloride shows a decrease in yield approximating 50 per cent. A 40 per cent decrease in yield is shown by 0.4 per cent of sodium sulfate in combination with 0.1 per cent sodium chloride. The reduction in yield is chiefly due to the sodium chloride rather than the sodium sulfate addition. This amount of sodium chloride when present alone in a soil shows no material effect on crop growth. This illustrates clearly an additive effect of these two salt concentrations each of which when present alone, shows a normal crop growth.

High concentrations of sodium sulfate accompanied by varying concentrations of sodium carbonate do not appear to influence crop growth until the concentration of sodium carbonate becomes greater than the maximum tolerance concentration for this salt. This is shown in graphs numbers 97, 129, 131.

In all salt combinations in which sodium sulfate predominates there is observed an additional toxicity due to sodium chloride, wherever it is present in the combination. This increased toxicity of sodium chloride is reduced by the presence of sodium carbonate concentrations that in themselves approach the maximum tolerance for this salt.

The above data present the first indication of a possible antagonism of ions when present in combinations in the soil solution. Much data are at hand on other crops that present clearer examples of possible antagonism of ions, hence a complete discussion of the effect of a combination of salts will be reserved until data on all crops are presented.

DISCUSSION OF THE EFFECT OF ALKALI SALTS ON A SECOND CROP OF WHEAT

All concentrations of sodium carbonate except the two highest, showed a marked stimulating effect on plant growth on the second crop. The highest concentration of added salt, namely, 0.9 per cent with a recovery of 0.31 per cent resulted in a total inhibition of growth.

With sodium chloride the smaller additions which showed stimulation in the first crop, show a slight decrease in yield in the second. In the higher additions where a decrease in crop growth was observed in the first crop, a stimulation occurs in the second. Generally speaking, the yield of the second crop varies inversely with the first crop, that is, if the first crop is low, the second is high, and vice versa.

The same observation holds with the sodium sulfate treatments as with sodium chloride. The higher treatments show a slight depression in the first crop and a large stimulation in the second. The greatest concentrations give the highest yield of wheat in the second crop.

TABLE 8

Salt recovery on fallow pots

POT NUMBER	TREATMENT			INITIAL SAMPLING				FIRST CROP				SECOND CROP			
	Na_2CO_3	NaCl	Na_2SO_4	Total equivalent Na_2CO_3	NaCl	Na_2SO_4	Total sodium salts	Total equivalent Na_2CO_3	NaCl	Na_2SO_4	Total sodium salts	Total equivalent Na_2CO_3	NaCl	Na_2SO_4	Total sodium salts
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
141A	Check			0.036	0.000	0.011	0.047	0.025	0.000	0.008	0.032	0.022	0.000	0.008	0.030
79A	0.20			0.096	0.000	0.005	0.101	0.087	0.000	0.010	0.097	0.065	0.000	0.009	0.074
81A	0.40			0.171	0.000	0.007	0.178	0.157	0.000	0.007	0.164	0.135	0.000	0.015	0.150
83A	0.60			0.231	0.000	0.006	0.237	0.231	0.000	0.007	0.238	0.204	0.000	0.022	0.226
85A	0.90			0.383	0.000	0.009	0.392	0.345	0.000	0.008	0.353	0.311	0.000	0.015	0.326
87A		0.10		0.036	0.067	0.008	0.111	0.028	0.100	0.006	0.134	0.020	0.127	0.012	0.159
89A		0.20		0.036	0.134	0.007	0.177	0.023	0.170	0.007	0.200	0.019	0.190	0.010	0.219
91A		0.40		0.036	0.254	0.006	0.296	0.025	0.364	0.005	0.394	0.025	0.373	0.009	0.407
93A			0.20	0.031	0.000	0.143	0.174	0.025	0.000	0.177	0.202	0.025	0.000	0.157	0.182
95A			0.40	0.031	0.000	0.306	0.337	0.028	0.000	0.446	0.474	0.020	0.000	0.364	0.384
97A			0.60	0.036	0.000	0.481	0.517	0.028	0.000	0.600	0.628	0.019	0.000	0.510	0.529
99A			0.90	0.029	0.000	0.697	0.726	0.020	0.004	0.835	0.859	0.020	0.000	0.850	0.870
101A	0.10	0.10		0.049	0.092	0.013	0.154	0.043	0.095	0.016	0.154	0.033	0.105	0.019	0.157
103A	0.30	0.05		0.128	0.052	0.007	0.187	0.110	0.047	0.006	0.163	0.098	0.058	0.012	0.168
105A	0.10	0.30		0.053	0.268	0.006	0.327	0.037	0.275	0.006	0.318	0.033	0.249	0.013	0.295
107A	0.60	0.10		0.227	0.100	0.000	0.327	0.188	0.082	0.017	0.287	0.188	0.096	0.027	0.311
109A	0.20	0.20		0.086	0.118	0.007	0.211	0.047	0.201	0.010	0.258	0.094	0.165	0.012	0.271
111A		0.05	0.20	0.031	0.046	0.191	0.268	0.027	0.040	0.045	0.112	0.022	0.045	0.195	0.262
113A		0.30	0.10	0.034	0.234	0.124	0.392	0.027	0.270	0.111	0.406	0.022	0.266	0.112	0.400
121A		0.10	0.40	0.029	0.062	0.302	0.393	0.020	0.102	0.370	0.492	0.017	0.100	0.382	0.499
123A		0.10	0.60	0.026	0.079	0.526	0.631	0.020	0.083	0.532	0.635	0.017	0.093	0.451	0.561
125A	0.10		0.10	0.057	0.000	0.091	0.148	0.043	0.000	0.092	0.135	0.034	0.000	0.083	0.117
127A	0.20		0.20	0.086	0.000	0.157	0.243	0.064	0.000	0.189	0.253	0.052	0.000	0.172	0.224

129A	0.30		0.40	0.129	0.000	0.332	0.461	0.103	0.000	0.307	0.410	0.094	0.000	0.388	0.482
131A	0.20		0.60	0.084	0.000	0.471	0.555	0.039	0.000	0.608	0.647	0.040	0.000	0.610	0.650
133A	0.60	0.05	0.10	0.242	0.000	0.082	0.324	0.150	0.000	0.100	0.250	0.209	0.000	0.088	0.297
135A	1.00	0.10	0.10	0.379	0.000	0.066	0.445	0.319	0.005	0.083	0.407	0.294	0.003	0.125	0.422
137A	0.05	0.10	0.05	0.039	0.053	0.076	0.168	0.029	0.031	0.051	0.115	0.022	0.063	0.045	0.130
139A	0.10	0.05	0.10	0.056	0.073	0.163	0.292	0.025	0.110	0.108	0.243	0.030	0.095	0.091	0.219
143A	0.20	0.10	0.10	0.095	0.091	0.122	0.308	0.063	0.058	0.086	0.207	0.052	0.088	0.142	0.282
145A	0.40	0.10	0.10	0.178	0.061	0.116	0.355	0.134	0.042	0.067	0.243	0.135	0.063	0.115	0.313
147A	0.60	0.05	0.20	0.245	0.098	0.189	0.532	0.194	0.077	0.151	0.422	0.172	0.098	0.178	0.548
24A	0.40	0.05	0.40	0.147	0.096	0.386	0.629	0.109	0.084	0.341	0.634	0.103	0.093	0.324	0.520
26A	0.20	0.05	0.40	0.079	0.034	0.442	0.555	0.052	0.032	0.356	0.440	0.052	0.063	0.439	0.554
2A	0.20	0.05	0.80	0.080	0.035	0.875	0.990	0.040	0.091	0.701	0.832	0.037	0.055	0.698	0.790
4A	0.05	0.05	0.60	0.034	0.037	0.724	0.795	0.018	0.022	0.516	0.556	0.025	0.036	0.464	0.523
12A	0.10	0.10	0.10	0.057	0.040	0.200	0.297	0.035	0.017	0.057	0.109	0.047	0.011	0.025	0.083
18A	0.40	0.20	0.60	0.121	0.065	0.453	0.639	0.068	0.044	0.401	0.513	0.098	0.045	0.208	0.351
31A	0.30	0.20	0.20	0.100	0.138	0.179	0.417	0.072	0.058	0.137	0.267	0.074	0.068	0.065	0.207
34A	0.10	0.20	0.20	0.053	0.106	0.199	0.358	0.025	0.072	0.175	0.272	0.034	0.088	0.073	0.195
75A	0.10	0.40	0.10	0.047	0.271	0.086	0.404	0.029	0.166	0.067	0.262	0.034	0.149	0.036	0.219

When the various combinations of salt additions are compared it is seen that whenever there has been a depression in the first crop yield, there is usually an increase in the second crop. The amount of increase is somewhat proportional to the amount of decrease in the yield in the first crop. The only combination which completely inhibited crop growth in both plantings is 1 per cent sodium carbonate and 0.1 per cent sodium sulfate, the 1 per cent sodium carbonate alone being sufficient to inhibit completely the growth of wheat.

The cause of the marked stimulating effect noted in the second crop yields, in all but the highest concentrations of alkali salts, will be discussed in detail when all the tolerance data are presented on other crops. This particular problem has been under investigation by the writers for some time. The possible reasons for this stimulation are many, namely, a rearrangement of soil bases, which in turn may result in the liberation of more available plant-foods; the favorable effect that certain alkali salts have on improving the physical conditions of soil; the effect on the bacterial flora of soils. All these studies have been under way and will be reported from this station at a later date. That all factors play a part in causing this stimulation is indicated by the results secured thus far. A recent publication by Greaves, Hirst and Lund (1) reporting leaching experiments corroborates the possibility of the liberation of plant-foods.

DISCUSSION OF THE TOTAL YIELD OF THE TWO CROPS

No discussion will be given on the effect of alkali salts on the total of the two crop yields for the reason that these crop yields compensate one another; the first crop showing a depression and the second, a stimulation. In order to secure more comparable total yields, all later tolerance studies have been carried out to include three or four crops. The total yields or their average, therefore, more truly represent the actual effect of added alkali salts on the yield of crops.

ALKALI RECOVERIES FROM FALLOWED AND CROPPED SOILS

As described in the plan of experiment a series of pots was prepared from each artificially prepared alkali soil and set aside to determine the effect of non-cropping as compared with cropping on the salt recovery. These pots were cared for in exactly the same manner as the duplicate pots on which crops were grown. They were sampled at the same periods as the wheat series.

An examination of the data shows considerable variation in the recoveries from the cropped and fallow pots. The general trend of the results, however, indicates that there is a persistent difference in the recovery of salts from the cropped and uncropped series.

The original alkali recoveries vary slightly for each of the triplicate pots. This is due to the difficulties, well known to those experienced in alkali soil studies, encountered in securing a uniform and equal distribution of alkali

salts throughout the soil as well as in sampling. For this reason conclusions should be based on the general average of results rather than on individual pots.

It is well known that a much smaller percentage of the added sodium carbonate can be recovered from a water extract of soil than with sodium chloride or sodium sulfate. The carbonate recoveries for the uncropped and cropped soils are both low, but the general trend of the results shows a lower recovery of the carbonate salts in the uncropped soils. This fact tends to show that under fallow conditions more carbonates are fixed or absorbed in the soil, and substantiates the conclusions drawn in a former publication (4) that carbonates undergo a change when added to a soil, being fixed as silicates or changed in form through a rearrangement of soil bases. With the cropped soils, more carbonate salts are recovered, due to the increased production of carbon dioxide which tends to prevent the fixing of the soluble carbonates into insoluble compounds.

The sodium chloride recoveries show more recoverable chloride in the fallow pots than in the cultivated crops. This may be partly due to the removal of a portion of the soluble chlorides by the crop growth.

There is considerable variation in the recoveries of the sulfate salts from the two series, showing, however, a slight tendency toward a lower recovery from the cropped soils which indicates some utilization of sulfates in crop growth.

THE EFFECT OF SALT CONCENTRATIONS ON RATE OF GERMINATION AND GROWTH

Data were secured on rate of germination, growth, and time of heading out for both crops. The data are so voluminous that only a general summary of the effect of the single salts and the combinations are given (table 3). The low concentrations of all single-salt additions showed very little effect on germination, rate of growth and time of heading out. The effect of high concentrations of the single salts is quite characteristic for each. Sodium chloride retards the germination at medium concentrations and at the highest concentrations used, the percentage of germination is materially lowered. When plants appear through the surface of the soil, the young plants grow very slowly and some die. If, however, they reach the height of 3 inches they usually continue to grow to maturity. The plants, however, grow rather spindling but are usually healthy looking and have a good color. The presence of sodium chloride in the soil hastens the heading out or fruiting period of the wheat.

For all concentrations except the extremely high ones sodium carbonate shows little retarding effect on germination. The highest concentrations do appreciably decrease the percentage of germination. The next two lower additions did not show an effect of inhibiting the germination, since the young plants quickly made their appearance. The effect of these concentrations was to kill the young plants as soon as they reached a height of approximately 3 to 5 inches. The appearance of the wheat plant when grown in low concentra-

tions of sodium carbonate is characteristic. The plant produces broad thick leaves and has an appearance slightly different from a wheat plant grown on a normal soil not containing alkali. In the higher concentrations, where plant growth is retarded, the wheat plants have an abnormal appearance, recognized by broad leaves, thick leaf sheaths and a stem which has a corroded appearance at the base. Sodium carbonate additions delay the heading out of the wheat.

Sodium sulfate additions were not large enough to kill the wheat plants. When other salts are present, with the high sulfate concentrations there is an effect similar to that shown by the sodium chloride treatments. These treatments speed up the heading out period and produce a spindling type of plant. Sodium sulfate showed practically no effect on rate or percentage of germination.

THE EFFECT OF ALKALI SALTS ON YIELD OF GRAIN

The effect of alkali salts on the yield of grain will not be discussed for the first crop, because it was grown during the winter months in the greenhouse. A lack of sunshine during this time delayed ripening. In addition, a mildew gained access to some of the plants during the latter period of growth, reducing grain yields. The second crop, however, was grown under more favorable conditions and very satisfactory grain yields resulted. In general the increase in grain yields parallels the increase of the total crop yields.

SUMMARY

First crop

Basing the observations on the recoverable rather than the added salts, the effects of alkali on the first crop of wheat are as follows:

Wheat was not affected by sodium carbonate until 0.1 per cent recoverable salt was found. At 0.2 per cent concentration there was evident toxicity; 0.3 per cent recoverable salt always resulted in a total crop failure.

Sodium chloride when present alone in the soil was not harmful to the growth of wheat until 0.2 per cent recoverable salt concentration was reached; 0.25 per cent recoverable sodium chloride showed a decided toxicity.

Recoveries of 0.75 per cent sodium sulfate failed to show any detrimental effect on crop yield. The tolerance for this concentration of sodium sulfate is materially decreased by the presence of 0.07 per cent of sodium chloride. In the presence of the same amount of sodium sulfate, sodium carbonate shows no effect until its own maximum tolerance limit of approximately 0.1 per cent is reached.

In combinations of sodium carbonate and sodium chloride, small recoveries of either salt had an influence on crop yield only when the other salt concentration approached its maximum tolerance.

Second crop

In the second crop, any toxic effect of the salts on plant growth is so effectively overshadowed by the stimulation of all treatments except the very highest carbonates, that no measurement of toxicity can be made. However, on other studies where more crops are grown on the same soil, this stimulation is overcome, and characteristic toxicities again become apparent.

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EFFECT OF IRON AND ALUMINUM SALTS ON THE PHOSPHORUS RECOVERY FROM SOILS AND QUARTZ SAND TREATED WITH TENNESSEE ROCK OR DOUBLE ACID PHOSPHATE

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INTRODUCTION

It has been shown in a previous paper (2) that different soils treated with either rock or acid phosphate allow certain phosphorus recovery by means of 0.2 N HNO$_3$; that this recovery from any particular soil is practically the same, regardless of whether phosphorus is applied in the form of double acid phosphate, or finely ground rock phosphate; and that the recovery of phosphorus from different soils, so treated, varies very greatly.

It was suggested in the paper referred to that this difference in phosphorus recovery from different soils may be due to the presence of iron and aluminum compounds with some additional influence from soluble silica and silicious compounds.

The present paper deals with the effect of adding ferric and aluminum chlorides in modifying the phosphorus recovery from some soils and sand, treated with phosphatic fertilizers.

EXPERIMENTAL

The general method followed in this study is the same as reported previously (2), namely; to 25 gm. of soil or sand was added a certain amount of FeCl$_3$ or AlCl$_3$ (in solid form); then a certain amount of either rock or double acid phosphate was added; the whole mass was thoroughly mixed, moistened with distilled water to about 60 per cent of saturation; then it was allowed to stand for 7 days at room temperature, after which it was taken up with 250 cc. 0.2 N HNO$_3$, shaken up for 3 hours, filtered and an aliquot taken for determination of phosphorus. In the phosphorus determination, the volumetric method was followed.

Three agricultural soils were used,—brown silt loam, brown gray silt loam, and black clay loam. These soils were of Champaign County, Illinois. Quartz sand, of a rather coarse texture, was used for comparison.

The ferric and aluminum chlorides were used in amounts equivalent to 0.1 and 0.2 gm. of salt per 25 gm. of soil or sand. The amount of phosphorus applied is indicated in the tables, and usually equalled 4 or 8 mgm.

of phosphorus. In one case, the same amount, 0.025 gm. of both phosphatic fertilizers was taken. Samples of soil or sand, treated with ferric or aluminum chloride, were left untreated with phosphates. This was done to see the effect of these salts on the phosphorus recovery from natural soil. In every case, the average of two determinations is hereby reported.

The results are summarized in tables 1, 2, 3, and 4, which are self-explanatory. The results as reported show the net amounts of phosphorus extracted from soils or sand, due to the added phosphorus. A blank to allow for the soil phosphorus was in each case previously subtracted and the relative efficiency of the phosphorus recovery was based on these net amounts.

TABLE 1

Extraction of phosphorus from 25 gm. of brown silt loam treated with either rock or acid phosphate containing 8 mgms. phosphorus

MATERIAL EXTRACTED WITH 0.2 N NITRIC ACID	PHOSPHORUS RECOVERY	
	Phosphorus obtained	Relative efficiency
	mgm.	*per cent*
Soil alone...	0.24	
Soil +0.1 gm. FeCl₃......................................	0.23	
Soil +0.2 gm. FeCl₃......................................	0.19	
Soil +0.1 gm. AlCl₃......................................	0.26	
Soil +0.2 gm. AlCl₃......................................	0.27	
Soil +0.050 gm. rock phosphate.........................	4.66	100
Soil + rock phosphate +0.1 gm. FeCl₃...................	4.16	89
Soil + rock phosphate +0.2 gm. FeCl₃...................	3.88	84
Soil + rock phosphate +0.1 gm. AlCl₃...................	4.78	102
Soil + rock phosphate +0.2 gm. AlCl₃...................	4.77	102
Soil + 0.0344 gm. acid phosphate.......................	4.41	100
Soil + acid phosphate +0.1 gm. FeCl₃..................	4.11	93
Soil + acid phosphate +0.2 gm. FeCl₃..................	4.08	93
Soil + acid phosphate +0.1 gm. AlCl₃..................	4.67	106
Soil + acid phosphate +0.2 gm. AlCl₃..................	4.78	108

The results obtained in this work, presented in tables 1, 2, 3, and 4, are rather interesting in as much as they show a considerable difference in effect produced by these two salts.

Ferric chloride added in these small amounts decreased the phosphorus recovery in every one of the three soils, the maximum decrease amounting to 16 per cent. Aluminum chloride, on the other hand, caused some stimulation of the phosphorus recovery in two of the three soils used. In the case of black clay loam, the increase was very pronounced, amounting, with 0.2 gm.

application, to 16 and 17 per cent with rock phosphate and double acid phosphate, respectively. In brown silt loam the stimulation was much less, and no stimulation was observed in brown gray silt loam. Neither ferric nor aluminum chloride had any influence on the phosphorus recovery in quartz sand

The results are noteworthy in connection with the fact that in agricultural literature dealing with the role of iron and aluminum in soil fertility, these two bases are often placed in one group as having many characteristics in common and influencing the soil solution in the same general direction. The

TABLE 2

Extraction of phosphorus from 25 gm. of brown gray silt loam treated with approximately 4 mgm. of phosphorus in the form of either rock or acid phosphate

MATERIAL EXTRACTED WITH 0.2 N NITRIC ACID	PHOSPHORUS RECOVERY	
	Phosphorus obtained	Relative efficiency
	mgm.	*per cent*
Soil alone..	0.47	
Soil +0.1 gm. FeCl$_3$..................................	0.41	
Soil +0.2 gm. FeCl$_3$..................................	0.40	
Soil +0.1 gm. AlCl$_3$..................................	0.49	
Soil +0.2 gm. AlCl$_3$..................................	0.52	
Soil rock phosphate..................................	3.42	100
Soil + rock phosphate +0.1 gm. FeCl$_3$....................	3.29	96
Soil + rock phosphate +0.2 gm. FeCl$_3$....................	3.07	90
Soil + rock phosphate +0.1 gm. AlCl$_3$....................	3.44	101
Soil + rock phosphate +0.2 gm. AlCl$_3$....................	3.46	101
Soil + acid phosphate................................	3.55	100
Soil + acid phosphate +0.1 gm. FeCl$_3$....................	3.35	94
Soil + acid phosphate +0.2 gm. FeCl$_3$....................	3.23	91
Soil + acid phosphate +0.1 gm. AlCl$_3$....................	3.51	99
Soil + acid phosphate +0.2 gm. AlCl$_3$....................	3.46	97

data from these experiments show that this is not always the case. In fact in their influence on the behavior of phosphorus in soils they are entirely different from one another. While iron inhibits the phosphorus going into solution, aluminum sometimes hastens it.

It should be noticed in this connection that the inhibitive action of ferric chloride does not have much of a residual effect. Indeed, what is held out of solution in the first of a series of extractions may be recovered with subsequent extractions. This was determined in an experiment with brown silt loam and brown gray silt loam in which five consecutive extractions of

phosphorus were made. After the first extraction was filtered and washed four times with distilled water the residue was treated with 250 cc. of fresh 0.2 N HNO$_3$, shaken up for 3 hours, filtered again and washed. This was repeated five times, and the results are summarized in tables 5 and 6.

The data are instructive. They show that ferric chloride causes a decrease in phosphorus recovery in the first extraction, but in the second extraction the residue yields a larger amount of phosphorus than from the untreated soil. Thus, at the end of the fifth extraction, there is nearly as much (or even more) phosphorus obtained as was present in the untreated

TABLE 3

Extraction of phosphorus from 25 gm. black clay loam treated with 0.025 gm. of either rock or acid phosphate

MATERIAL EXTRACTED WITH 0.2 N NITRIC ACID	PHOSPHORUS RECOVERY	
	Phosphorus obtained	Relative efficiency
	mgm.	*per cent*
Soil alone	0.96	
Soil +0.1 gm. FeCl$_3$..	0.69	
Soil +0.2 gm. FeCl$_3$..	0.66	
Soil +0.1 gm. AlCl$_3$..	0.83	
Soil +0.2 gm. AlCl$_3$..	0.90	
Soil + rock phosphate...................................	2.01	100
Soil + rock phosphate +0.1 gm. FeCl$_3$.....................	1.87	93
Soil + rock phosphate +0.2 gm. FeCl$_3$.....................	1.72	86
Soil + rock phosphate +0.1 gm. AlCl$_3$.....................	2.11	105
Soil + rock phosphate +0.2 gm. AlCl$_3$.....................	2.24	117
Soil + acid phosphate...................................	2.44	100
Soil + acid phosphate +0.1 gm. FeCl$_3$.....................	2.27	93
Soil + acid phosphate +0.2 gm. FeCl$_3$.....................	1.98	81
Soil + acid phosphate +0.1 gm. AlCl$_3$.....................	2.68	110
Soil + acid phosphate +0.2 gm. AlCl$_3$.....................	2.84	116

soil. Taking all five extractions together, one notices that the amount of recovered phosphorus runs pretty much alike in all cases.

It was observed, as one notices in table 4, that neither ferric nor aluminum chlorides had any influence on the phosphorus recovery in quartz sand. The sand behaved very unlike the agricultural soils in this respect.

However, being void of any soluble salts in appreciable amounts, sand affords a very convenient medium for study. This particular sand was rather coarse in texture to resemble agricultural soil. For this reason, 25 gm. portions of silica flour, passing through a 200-mesh sieve, were treated with

0.5 gm. $FeCl_3$, $AlCl_3$ and $CaCO_3$, singly and in various combinations About 4 mgms. of phosphorus in the form of rock phosphate was added to this silica flour and wetted. The phosphorus extraction and determination were made as usual.

A 10-cc. aliquot of extracted solution, immediately after filtering, was taken and titrated against a standard alkali. This was done, in order to ascertain to what extent the reduction in acidity of the extractor influences the amount of phosphorus extracted from silica flour treated with different salts.

TABLE 4

Extraction of phosphorus from 25 gm. of quatz sand treated with approximately 4 mgm. phosphorus in the form of either rock or acid phosphate

MATERIAL EXTRACTED WITH 0.2 N NITRIC ACID	PHOSPHORUS RECOVERY	
	Phosphorus obtained	Relative efficiency
	mgm.	*per cent*
Sand alone...	0.04	
Sand +0.1 gm. FeCl₃...................................	0.01	
Sand +0.2 gm. FeCl₃..................................	0.02	
Sand +0.1 gm. AlCl₃...................................	0.06	
Sand +0.2 gm. AlCl₃...................................	0.07	
Sand + rock phosphate................................	3.73	100
Sand + rock phosphate +0.1 gm. FeCl₃.................	3.77	101
Sand + rock phosphate +0.2 gm. FeCl₃.................	3.67	98
Sand + rock phosphate +0.1 gm. AlCl₃.................	3.64	98
Sand + rock phoshpate +0.2 gm. AlCl₃.................	3.78	101
Sand + acid phosphate................................	3.67	100
Sand + acid phosphate +0.1 gm. FeCl₃.................	3.68	100
Sand + acid phosphate +0.2 gm. FeCl₃.................	3.80	103
Sand + acid phosphate +0.1 gm. AlCl₃.................		
Sand + acid phosphate +0.2 gm. AlCl₃.................	3.77	103

The results showing the percentage of phosphorus recovery, and the percentage of the original acidity in the resultant solution, are presented in figure 1. The results with this extremely fine quartz sand, or flour, correspond to those obtained with coarser quartz sand in that neither ferric chloride nor aluminum chloride, added alone, show any appreciable influence on the phosphorus recovery as compared with sand that had not been treated with these salts. The mixture of calcium carbonate and aluminum chloride was also without any influence, the recovery being 98.2 per cent of the check. Other mixtures, however, showed some inhibitive effect.

Thus, a mixture of calcium carbonate and ferric chloride reduced the recovery to about 89 per cent of the check, and the mixture of ferric chloride and aluminum chloride reduced the phosphorus recovery to 93.6 per cent. The mixture of calcium carbonate, ferric chloride and aluminum chloride cause a reduction to 92.3 per cent of the check.

TABLE 5

Residual effect of 0.2 gm. of iron or aluminum chloride on the extraction of phosphorus from 25 gm. brown silt loam, treated with approximately 4 mgm. phosphorus in the form of either rock or acid phosphate

Extraction with 0.2 N nitric acid was repeated 5 times

	PHOSPHORUS RECOVERY						RELATIVE VALUE OF FIRST EXTRACTION	RELATIVE VALUE OF TOTAL EXTRACTION
	1st extraction	2nd extraction	3rd extraction	4th extraction	5th extraction	Total		
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*		
Rock phosphate.............	1.86	0.47	0.24	0.13	0.09	2.79	100	100
Rock phosphate and FeCl₃.....	1.52	0.57	0.26	0.12	0.06	2.53	82	91
Rock phosphate and AlCl₃......	1.95	0.38	0.18	0.09	0.03	0.63	105	94
Acid phosphate..............	1.75	0.46	0.21	0.12	0.02	2.56	100	100
Acid phosphate and FeCl₃......	1.52	0.57	0.27	0.15	0.06	2.57	87	100
Acid phosphate and AlCl₃......	1.86	0.38	0.21	0.09	0.00	2.54	106	99

TABLE 6

Residual effect of 0.2 gm. of iron or aluminum chloride on the extraction of phosphorus from 25 gm. brown gray silt loam treated with approximately 4 mgm. phosphorus in the form of either rock or acid phosphate

Extraction with 0.2 N nitric acid was repeated five times

	PHOSPHORUS RECOVERY						RELATIVE VALUE OF FIRST EXTRACTION	RELATIVE VALUE OF TOTAL EXTRACTION
	1st extraction	2nd extraction	3rd extraction	4th extraction	5th extraction	Total		
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*		
Rock phosphate.............	3.02	0.25	0.09	0.02	0.00	3.38	100	100
Rock phosphate and FeCl₃......	2.55	0.72	0.16	0.06	0.03	3.52	84	104
Rock phosphate and AlCl₃......	3.02	0.42	0.11	0.05	0.01	3.61	100	107
Acid phosphate..............	3.10	0.24	0.10	0.05	0.01	3.50	100	100
Acid phosphate and FeCl₃......	2.84	0.56	0.16	0.05	0.01	3.62	92	103
Acid phosphate and AlCl₃......	3.10	0.26	0.09	0.04	0.01	3.50	100	100

In these cases the acidity of the resultant extraction solution was a very insignificant factor in modifying the phosphorus recovery, as one notices in figure 1. Taking silica flour treated with phosphorus alone, a standard or a check, calcium carbonate alone reduced the strength of the acid without reducing the phosphorus recovery. Silica treated with ferric chloride(alone)

showed an increase in acidity. In both of these cases the recovery stood practically unchanged or slightly reduced. With a reduction in acidity in the silica treated with ferric chloride and calcium carbonate, the reduction of phosphorus recovery was very pronounced. The extreme case was observed in silica treated with ferric and aluminum chlorides, where a considerable depression in phosphorus recovery was accompanied by the greatest acidity in the extraction solution. Other forces, evidently, were at work that influenced the phosphorus recovery to a greater extent than the change in the acidity strength.

Just what takes place when any of these salts are present with the phosphatic fertilizer, is difficult to say. In the presence of iron, ferric phosphate
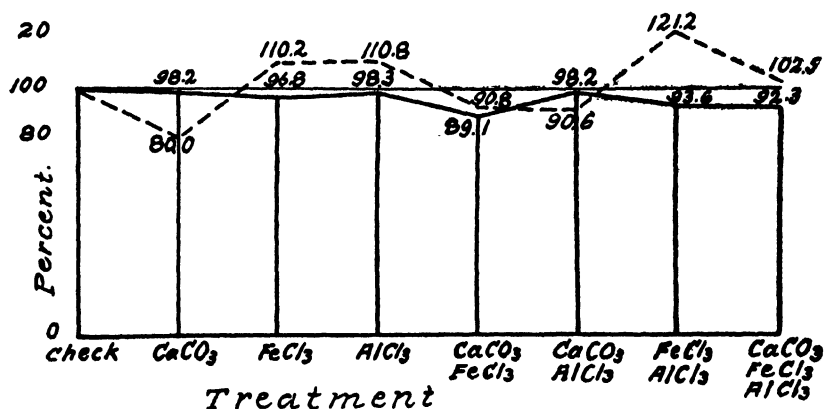
FIG. 1. EFFECT OF FERRIC CHLORIDE, ALUMINUM CHLORIDE AND CALCIUM CARBONATE SINGLY AND IN DIFFERENT COMBINATIONS, ON THE PER CENT OF PHOSPHORUS RECOVERY BY MEANS OF 0.2N HNO₃ FROM FINE SILICA FLOUR TREATED WITH FINELY GROUND ROCK PHOSPHATE

Heavy solid line represents values in phosphorus recovery expressed in percentage of that in check.

The broken line represents values of acidity in resultant extracted solution expressed in percentage of that in check.

is undoubtedly formed. A similar salt is formed with aluminum. An excess of calcium would tend toward the formation of tricalcium phosphate. These salts, however, go into solution on shaking for 3 hours in 0.2 N HNO₃ to the extent of 95–98 per cent, as reported previously (2). This is substantiated in the present experiment. When iron and aluminum are present together, the phosphorus recovery is inhibited. Could it be possible that a double phosphatic salt of iron and aluminum is formed, which would be more stable than either ferric or aluminum phosphate alone?

The perusal of chemical textbooks and reference books on the subject failed to locate any evidence that a double salt of this composition was ever recorded. The data here obtained, however, tend to show that this might

be the case when both of these elements are present in a position for any regrouping in the molecular structure of their respective salts.

It is a well known fact that some double salts are even more soluble than the respective single salts entering into their composition. For instance ferrous sulfate (1) has a solubility in water of 20.85 per cent at 10°C. Potassium sulfate, at the same temperature, has a solubility in water to the extent of 9.22 per cent. Ferrous potassium sulfate, however, at the same temperature dissolves in water to the extent of 24.5 per cent, showing that more sulfur will be in solution in the double salt than in either of the two single salts. On the other hand, there are salts whose solubility decreases when they form a double salt. Thus, aluminum potassium sulfate is less soluble, taking sulfur as a unit of measure, than aluminum sulfate, and potassium sulfate taken separately. Their respective solubilities per 100 gm. of water at 10°C. is as follows: aluminum potassium sulfate, 7.60 gm.; aluminum sulfate, 33.5 gm.; potassium sulfate, 9.22 gm. In this particular case, the decrease in solubility on forming a double salt is very pronounced. In case of a change from potassium sulfate to potassium alum, the decrease in solubility equals 18 per cent, while from aluminum sulfate to potassium alum, the decrease is 77 per cent. The latter decrease in solubility is much greater than that reported in the present study with iron and aluminum phosphates.

It stands to reason, therefore, that such a double salt of ferric aluminum phosphate is being formed and evidently it is more stable in its molecular structure than its component single salts. The molecular structure of iron phosphate is generally presented as follows:

$$Fe{\underset{\diagdown O}{\overset{\diagup O}{\lessgtr}}}O{\rightarrow}P{=}O$$
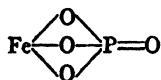
A similar structure is also conceivable for aluminum phosphate.

To form a double salt the elements may regroup themselves somewhat as follows:

$$Fe{\underset{\diagdown O}{\overset{\diagup O}{\lessgtr}}}O{\rightarrow}P{\overset{\diagup O}{\underset{\diagdown O}{\lessgtr}}}P{\underset{\diagdown O}{\overset{\diagup O}{\lessgtr}}}O{\rightarrow}Al$$
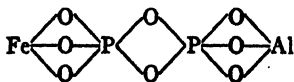
It is very reasonable to suppose that such a double salt of phosphate would be more stable, on account of the locking of oxygen between two phosphorus atoms, than the single phosphate of either iron or aluminum.

Turning our attention to tricalcium phosphate, and to the formation of double phosphate with iron, the respective structural formula may assume the following forms:

$$Ca_3(PO_4)_2 = Ca\diamondsuit P=O \ \ Ca\diamondsuit \ \ Ca\diamondsuit P=O$$

$$Fe_2Ca_3(PO_4)_4 = Ca\diamondsuit P \diamondsuit P{-}O{-}Fe \ \ Ca\diamondsuit \ \ Ca\diamondsuit P \diamondsuit P{-}O{-}Fe$$
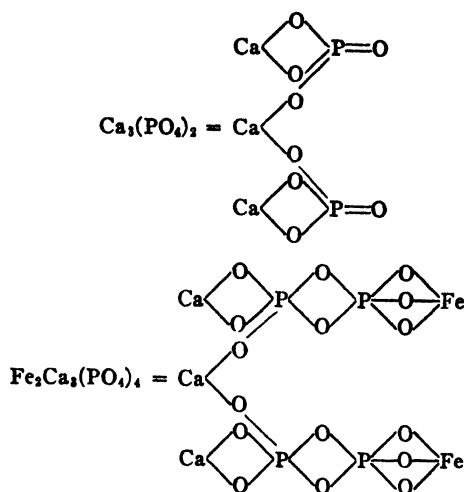
The suggestion above offers a plausible explanation of the results obtained with soil and silica flour treated with various salts here recorded. It explains why there was a difference in the phosphorus recovery from phosphate treated soils as reported in previous paper (2). There are nearly always present soluble salts of either calcium or aluminum, or both, one of which might form a double salt with the iron, and thus reduce the phosphorus availability in phosphorus treated soil. On addition of more ferric chloride, iron would tend to dominate the regrouping of phosphorus molecules, thus still further reducing the phosphate recovery.

Soil silicates, soluble in 0.2 N HNO_3, may contribute considerably to the results here obtained. Similarly, silicates present in soils in colloidal solutions, may have similar effect on the solubility of phosphates.

The data presented above suggest the following practical consideration. In order to utilize soil phosphorus or phosphorus from an applied phosphatic fertilizer, a given soil should be managed in such a way that it will not have iron in a soluble form to any appreciable extent. This would tend largely to prevent the formation of the extremely insoluble iron aluminum phosphate. Such a favorable condition would be maintained if the soil solution is kept at about its neutrality. Natural soil acidity tends to render the iron and aluminum more soluble, thus increasing the danger of locking of the available phosphorus in the form of double phosphate of iron and aluminum. On the other hand, a large amount of calcium carbonate in the soil tends to neutralize the soil-forming acids so quickly and so completely that the phosphorus availability becomes inhibited (2, p. 54).

Turning attention to aluminum chloride, one notices that its effect in no way resembles that of iron chloride. Present alone, aluminum chloride in silica flour has no effect on the phosphorus recovery. Present in combination with calcium carbonate, it is also without any appreciable influence.

Upon adding a small amount of this salt to soils, it had even a stimulating effect on the phosphorus recovery in two of the three soils studied. It is evident that in this respect aluminum salts have properties very unlike those observed in salts of iron. If it forms double phosphate with calcium, the behavior of this compound is not similar to that formed by iron and calcium.

In conclusion, it should be noted that in all respects, phosphorus behaved in soil, as well as in sand, in precisely the same way regardless of the source of phosphorus; that is to say, the phosphorus recovery was no greater from double acid phosphate than from finely ground Tennessee rock phosphate.

SUMMARY

1. Ferric chloride on addition to three different soils caused a decrease in phosphorus recovery by means of 0.2 N HNO_3, phosphorus being previously applied to the soil in the form of either Tennessee rock phosphate or double acid phosphate.

2. Aluminum chloride, applied to the same soils, showed no depressive effect on the phosphorus recovery. On the contrary, in two out of three cases, it slightly increased the phosphorus recovery.

3. When either $CaCO_3$, $FeCl_3$ or $AlCl_3$ was applied to fine silica flour (all passing through a 200-mesh sieve) treated with rock phosphate, it did not significantly affect the phosphorus recovery. The application of a mixture of $CaCO_3$ and $FeCl_3$, of $FeCl_3$ and $AlCl_3$, and also of $CaCO_3$, $FeCl_3$ and $AlCl_3$, caused some decrease in the phosphorus recovery. The influence of application of a mixture of $CaCO_3$ and $AlCl_3$ was much smaller in this respect.

4. It is suggested that double salts of phosphates may be formed; in some cases they may be less soluble than the corresponding single salts. $FeAl(PO_4)_2$ may be somewhat more insoluble than either $FePO_4$ or $AlPO_4$. Structural formulas harmonizing with this hypothesis are suggested.

5. In repeated extractions with fresh nitric acid, phosphorus from iron treated soil goes into solution. In five consecutive extractions, practically the same amount of phosphorus was extracted, whether the initial treatment was iron chloride or aluminum chloride.

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(2) WOLKOFF, M. I. 1924 Relative availability of the phosphorus of raw rock phosphate and acid phosphate in soils. *In* Soil Sci., v. 17, p. 39–56.

SYNTHETIC CALCIUM SILICATES AS A SOURCE OF AGRICULTURAL LIME: I. A COMPARISON OF THE INFLUENCE OF SYNTHETIC CALCIUM SILICATES WITH OTHER FORMS OF LIME AS AFFECTING PLANT GROWTH [1]

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INTRODUCTION

From data obtained by numerous investigators, there is good reason to doubt the superiority of one liming material over another when the different materials are applied on an equivalent CaO basis. Therefore, the selection of a liming material by the individual must be an economic one, depending largely on the price of the various materials and their relative content of lime or other bases; the distance of the haul, etc. Frear (5) and Kopeloff (8) give reviews of the extensive literature on the comparison of the various liming materials in their effects upon plant growth.

The literature relative to the use of silicates as carriers of bases for the soil is not so extensive. Grégoire (6) found from water-culture experiments that calcium and sodium zeolites stimulated both root and aërial development of rye. Mieth (11) observed that the calcium of various lime silicates was available to oats grown in water cultures.

MacIntire and Willis (10) compared silicates and carbonates as sources of lime and magnesia for plants in pot studies and came to the conclusion that the mineral calcium and magnesium silicates, wollastonite and serpentine, were very beneficial when applied either singly or jointly. The natural calcium silicate proved decidedly superior to an equivalence of calcium carbonate. However, these investigators used applications of calcium carbonate as high as 16,070 pounds above the requirement as estimated by the Veitch method. They likewise attribute the long continued effects of liming in small or moder-

ate amounts to a conservation of the lime as silicates in the soil. Ames (1) reports pot experiments comparing basic slag, calcium carbonate, and a calcium silicate on the growth of clover on soil from the Wooster farm. The soil gave a good growth of clover without treatment, but the calcium silicate showed an increase of 42.6 per cent over the untreated soil. The materials were each applied at the rate of 4400 pounds per acre. Cowles (4) and Scheidt (12) report the results of vegetation experiments on an acid soil which had been treated with calcium carbonate, calcium hydrate, and di-calcium silicate on an equivalent CaO basis. From a number of tests with numerous plants, the authors came to the conclusion that di-calcium silicate was superior to the other forms of lime used, attributing the superior results obtained partly to the silica content of the di-calcium silicate. The di-calcium silicate used by these investigators is the same as that employed in the studies reported in this paper. Hartwell and Pember (7) studying the same silicate, arrive at the conclusion that it is as effective as limestone in overcoming the toxic conditions in an acid soil, but that there is no justification in claiming additional value because of the silica content of the material.

Connor (2) used a calcium silicate (Ca_2SiO_4) on an acid black sand soil and obtained greater crops of beets, corn, and oats than from an equivalent amount of calcium hydrate. He explained the beneficial effects of the silicate as due to the insolubility of the aluminum silicate derived from the silicate as compared with the aluminum hydrate formed on the addition of calcium hydrate. Field tests reported in the same paper show that the calcium silicate compared quite favorably with limestone in correcting the unfavorable conditions for the growth of oats, hay, and corn on a soil at Wanatan. Schollenberger (13) from a series of pot tests with laboratory-prepared calcium silicate obtained increased crop yields and results superior to those obtained from additions of calcium carbonate.

From the fore-going résumé of the literature of the subject, it may be concluded that calcium and magnesium in the form of silicates are active for the correction of the soil condition called "acid," and are therefore beneficial to plant growth.

With these previously conducted experiments in mind, the value of two synthetically prepared calcium silicates as carriers of agricultural lime has been investigated. A comparison of these silicates with other carriers of lime has been made at the New Jersey Agricultural Experimental Stations. The results will be presented in three papers, the first of which deals with the influence of the synthetic calcium silicates upon plant growth, the subsequent papers being an attempted analysis of the factors contributing to the influence on plant growth.

DESCRIPTION OF SILICATES

So-called "di-calcium silicate" $(CaO)_2SiO_2$ is a product prepared in a process described by Cowles (3). The product contains about 80 per cent di-calcium

silicate and relatively large percentages of sodium and aluminium compounds as impurities.

The second silicate—called "limosil" for lack of a better name—is prepared in a process for the recovery of potash from glauconite. One description of this process is given by Shreve (14). From the nature of the reaction between calcium hydrate and glauconite, the inventors of the process are under the impression that a mono-calcium silicate is formed. Beside the mono-calcium silicate, the material contains about 13 per cent free lime in the form of calcium hydrate. However, analyses show that upon drying and standing the calcium hydrate becomes slowly carbonated.

The following are typical analyses of these synthetic silicates:

	DI-CALCIUM SILICATE	LIMOSIL
	per cent	*per cent*
Silica (SiO_2)	30.34	25.62
Iron oxide (Fe_2O_3)	2.03	9.02
Calcium oxide (CaO)	49.14	40.95
Free lime		13.05
Magnesium oxide (MgO)	3.26	
Sodium oxide	6.01	
Alumina (Al_2O_3)	7.07	
Total potash (K_2O)		1.90
Soluble potash		0.23
Phosphoric acid (P_2O_5)		0.14

These silicates have been compared with other forms of lime in a number of pot and field experiments the results of which follow. Due to the relatively large number of tests conducted, the averaged results are usually given, thus eliminating a great mass of data which would otherwise be very ineffectively handled.

EXPERIMENTAL RESULTS AND DISCUSSION

Series I

The comparative effects of ground limestone, calcium hydrate, and di-calcium silicate on plant growth in a loam soil were tested by the ordinary pot-culture method. The pots used were glazed inside and out and were of two sizes—18- and 10-pound capacities. The soils used were removed from plot N and plot 11A of the unlimed series of the New Jersey Experiment Station plots. A description of the soil from plot 11A, together with the fertilizer and cultural treatments, has been reported in Bulletin 260 (9) of the New Jersey Station. The soil represented by plot N has received no commercial nitrogen for more than ten years. It has not been limed for a longer period, possibly 20 or 25 years. It has received annual applications of acid phosphate at the rate of 300 to 400 pounds, and muriate of potash at the rate of 100 to 200

pounds per acre for the past 15 years. The soil showed a lime requirement by the Veitch method of 2000 pounds of CaO per acre at the time of removal in 1920. The soil of plot 11A has received applications of acid phosphate, muriate of potash and ammonium sulphate since 1908 and showed a lime requirement by the Veitch method of slightly over 2000 pounds of lime (CaO) per acre when removed from the plot in 1920.

After removal from the plots, the soil was screened, thoroughly air-dried, and weighed into tared pots. The liming materials[4] were carefully weighed and were thoroughly mixed throughout the entire mass of soil before the addition of water. All materials were applied at the rate of 2000 pounds of CaO per acre of 2,000,000 pounds. A moisture content of 60 per cent of the maximum water-holding capacity (Hilgard) was maintained throughout the experiment.

Duplicate pots of the soil from plots N and 11A were seeded to soybeans, barley, and buckwheat on October 16, 1920, and on November 1, 1920, respectively. When the seedlings were well above the ground they were thinned to a constant number per pot: 6 of soybean, 12 of barley, and 8 of buckwheat. The plants of plot-N group were harvested after $9\frac{1}{2}$ weeks and those of the plot-11A group, after 13 weeks. No attempt was made to remove the roots from the soil. The dried plants were milled to a fine powder and the nitrogen-content determined by the Kjeldahl method. After the first crop, 2 gm. of acid phosphate, 2 gm. of dried blood and 1 gm. of potassium chloride were mixed throughout the soil. In each pot 8 plants of buckwheat were grown.

The relative dry weights and total nitrogen results are given in tables 1 and 2 respectively.

The soybean showed practically the same response to ground limestone, di-calcium silicate and calcium hydrate. However, the di-calcium silicate proved distinctly superior for the buckwheat which followed the soybeans grown on the soil from plot 11A. On both soils di-calcium silicate was distinctly beneficial to barley. This may be attributed to the reactivity of the added silica. The silicate also appears to be superior to the other forms of lime as judged by the yield of buckwheat following the barley on both soils. Calcium hydrate proved to be more effective upon the first crop of buckwheat, but for 2 successive crops of buckwheat, the di-calcium silicate was superior on both soils, especially on the soil from plot 11A. When the relative yields of all the crops are averaged, the di-calcium silicate proves to be the more effective on both soils. On the soil from plot N, the calcium hydrate and ground limestone gave practically the same results, however on the more acid soil from plot 11A the calcium hydrate proved better than ground limestone. The averaged relative yield of all crops on both soils shows that di-calcium silicate is more efficacious

[4] Analyses of materials used:

	CaO per cent
Ground limestone	52.41
Di-calcium silicate	44.52
Calcium hydrate	72.95

than is calcium hydrate in overcoming the unfavorable condition in the so-called "acid" soils, while the hydrate proved more effective than ground limestone.

The nitrogen content of the plants grown in the unlimed soils was higher than of those grown in the limed soils in every case except that of buckwheat

TABLE 1

Relative dry weights of soybeans, barley and buckwheat grown on soils from plot N and plot 11A treated with ground limestone, di-calcium silicate and calcium hydrate

TREATMENT	SOYBEAN FOLLOWED BY BUCKWHEAT		BARLEY FOLLOWED BY BUCKWHEAT		BUCKWHEAT FOLLOWED BY BUCKWHEAT		AVERAGED RELATIVE YIELD, ALL CROPS	AVERAGED RELATIVE YIELD, FIRST 3 CROPS, BOTH SOILS	AVERAGED RELATIVE YIELD, ALL CROPS, BOTH SOILS
	Soybean	Buckwheat	Barley	Buckwheat	Buckwheat	Buckwheat			
Loam soil from plot N†									
No lime	(2.06 gm.) 100.0	(6.09 gm.) 100.0	(2.02 gm.) 100.0	(7.09 gm.) 100.0	(1.71 gm.) 100.0	(2.64 gm.) 100.0	100.0	100.0	100.0
* 16.3 gm. ground limestone	324.3	255.9	442.4	192.6	341.5	595.5	358.7	494.8	574.0
* 19.2 gm. di-calcium silicate	347.9	247.9	719.8	229.2	359.3	663.9	428.0	614.5	713.8
* 11.7 gm. calcium hydrate and 4.27 gm. hydrated silica	328.9	243.8	530.5	196.3	445.0	622.4	394.5	576.5	624.8
Loam soil from plot 11A‡									
No lime	(1.68 gm.) 100.0	(1.27 gm.) 100.0	(1.50 gm.) 100.0	(1.54 gm.) 100.0	(0.74 gm.) 100.0	(0.69 gm.) 100.0	100.0		
*9.06 gm. ground limestone	519.7	1,081.9	248.0	561.6	1,093.2	1,231.2	789.3		
* 10.66 gm. di-calcium silicate	509.8	1,343.9	420.1	850.8	1,330.4	1,539.7	999.1		
* 6.50 gm. calcium hydrate	529.9	1,090.5	262.0	589.3	1,362.8	1,296.0	855.1		

* Equivalent to 2000 pounds of CaO per acre.
† Eighteen pounds of soil per pot.
‡ Ten pounds of soil per pot.

from 11A. However, the total nitrogen recovery in the limed crop exceeded that of the control because of greatly increased yields. The percentage of nitrogen in the soybeans grown on the untreated soil from plot 11A is higher than the results obtained by other investigators. However, the percentages of nitrogen are in accordance with those obtained by Voorhees and Lipman (15). These investigators, state:

As time went on the lack of available phosphoric acid was felt more and more in the soils of series 1 and the amount of available nitrogen present became greater than the minimum required for the production of the corresponding amounts of dry matter. As a necessary consequence of this situation, the dry matter of series 1 contained what may be termed an abnormally high proportion of nitrogen.

Under the conditions of the present experiment, there should be no deficiency of phosphoric acid or potash. It is conceivable, however, that there can be present in the soils a greater proportion of available nitrogen than is neces-

TABLE 2

Relative total nitrogen content of soybeans, barley, and buckwheat grown on soils from plot N and from plot 11A untreated, and treated with various liming materials

TREATMENT	RELATIVE TOTAL NITROGEN CONTENT			AVERAGED RELATIVE TOTAL NITROGEN CONTENT			AVERAGED RELATIVE TOTAL NITROGEN CONTENT, ALL CROPS	AVERAGED RELATIVE TOTAL NITROGEN CONTENT, ALL CROPS ON BOTH SOILS
	Soybean	Barley	Buckwheat	Soybean	Barley	Buckwheat		
Loam soil from plot N								
	(0.09 gm.)	(0.06 gm.)	(0.032 gm.)					
No lime..................	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
* 16.3 gm. ground limestone...	259.3	437.5	433.0	267.5	279.1	633.4	376.6	393.3
‡ 19.2 gm. di-calcium silicate...	280.7	491.1	514.6	265.9	338.8	782.3	428.8	467.3
* 11.7 gm. calcium hydrate and 4.27 gm. hydrated silica.....	277.5	350.6	549.5	247.3	246.7	707.4	392.6	399.4
Loam Soil from plot 11A								
	(0.09 gm.)	(0.03 gm.)	(0.014 gm.)					
No lime..................	100.0	100.0	100.0				100.0	
* 9.06 gm. ground limestone..	275.6	120.6	833.7				409.9	
* 10.66 gm. di-calcium silicate..	250.2	186.5	1,080.9				505.8	
* 6.50 gm. calcium hydrate...	217.0	142.8	865.2				406.3	

* Equivalent to 2000 pounds of lime (CaO) per acre.

sary for the production of the small growth obtained under the unfavorable condition, whether this unfavorable condition be considered as due to the so-called "acidity" or to a lack of calcium. The fact that the plants took up a large proportion of nitrogen under these conditions may indicate a deficiency of one or more basic elements.

Eleven of the 18 relative total nitrogen recoveries coincided with the order of relative yield of dry matter.

Series II

In this series of pot cultures, 3 soils were used. The first soil was obtained from plot 11A of the New Jersey Experiment Station plots described above. The second a loam soil designated as "Sassafras loam" was from an old field near the College Farm. It had not received an application of lime within the last 20 years, having been under sod for a period of years, and showed a lime requirement by the Veitch method of 2000 pounds of CaO per foot-acre of 2,000,000 pounds. The third soil was a Penn loam obtained from a well-limed and flourishing alfalfa field and showed no lime requirement by the Veitch method.

The air-dried soils were passed through a ¼-inch mesh sieve and 10-pound portions were weighed into glazed pots, duplicate pots being used for each treatment. The liming materials[b] were sieved to the same fineness and incorporated with the soil before water was added. Each pot received an application of acid phosphate at the rate of 600 pounds and muriate of potash at the rate of 200 pounds per acre. The soils were brought to 60 per cent of their respective water-holding capacities and maintained at this point by the addition of distilled water.

The experiment called for: First, a comparison of a 2000-pound CaO-equivalence of limosil, ground limestone, calcium hydrate and di-calcium silicate on all soils; second, a comparison of 500-, 1000-, 2000-, and 4000-pound CaO-equivalence of limosil. Three crops; soybeans, barley, and corn, were grown in order. After the removal of each crop the soil was stirred, screened and placed again in the pots. Only one application of lime or fertilizing salts was made, and the same number of plants were grown in each pot. The soybeans were planted on May 5, 1921, and harvested 9 weeks later; barley was planted on August 22, and harvested after 17 weeks; corn was planted on January 4, 1922, and harvested 6 weeks later. The dry weights of the plants were obtained by drying at 100°C. for several days. The total and relative dry weights of the crops produced on the various soils under the treatments are given in table 3.

The comparison of the materials on the equivalent lime basis indicates that the silicates are as effective as the other forms of lime. Considering the percentage of error in this type of experimentation the fact is emphasized that one type of lime is equally effective with the others in overcoming the deleterious effects of a so-called "acid" soil on plant growth.

The total dry weight of the crops increased with the application of the limosil for all 3 soils. The greatest relative increases were obtained with the

[b] Analyses of materials used:

	CaO per cent
Ground limestone	56.52
Calcium hydrate	75.28
Di-calcium silicate	50.93
Limosil	40.95

very acid soil from plot 11A. However, the Sassafras loam shows an increase which is well above the error of experimentation. Even the yields on the previously limed Penn loam show a perceptible increase over those from the untreated soil.

Series III

The comparative effects of calcium oxide, calcium hydrate, ground limestone, di-calcium silicate and limosil on the growth of soybeans and buckwheat in 2 acid soils were studied by the ordinary pot method. The first soil was the Sassafras loam obtained from an old field and described under series II. The

TABLE 3

Total dry weights and relative total dry weights of 3 crops grown on soils from plot 11A, Sassafras loam, and Penn loam treated with increasing amounts of limosil, and with calcium hydrate, di-calcium silicate, ground limestone, and limosil on an equivalent lime basis

TREATMENT	EQUIVALENT AP-PLICATION OF CaO PER ACRE	TOTAL DRY WEIGHT OF 3 CROPS*			RELATIVE TOTAL DRY WEIGHT OF 3 CROPS			AVERAGED RELA-TIVE TOTAL DRY WEIGHT
		Soil from plot 11A	Sassa-fras loam	Penn loam	Soil from plot 11A	Sassa-fras loam	Penn loam	
	pounds	*gm.*	*gm.*	*gm.*				
No lime....................		4.24	9.16	12.46	100.0	100.0	100.0	100.0
2.769 gm. limosil............	500	16.90	14.62	12.68	398.4	159.6	101.8	219.9
5.538 gm. limosil............	1,000	19.08	15.99	13.52	449.8	174.5	108.5	244.9
11.076 gm. limosil............	2,000	25.14	17.52	13.54	592.6	191.2	108.7	297.5
22.152 gm. limosil............	4,000	29.23	22.71	15.08	689.8	247.8	121.0	352.5
11.076 gm. limosil............	2,000	25.14	17.52	13.54	592.6	191.2	108.7	297.5
8.024 gm. ground limestone....	2,000	26.69	18.57	12.97	629.2	202.6	104.1	311.9
6.026 gm. calcium hydrate....	2,000	27.91	17.16	13.71	657.8	187.2	110.1	318.4
8.904 gm. di-calcium silicate...	2,000	25.70	20.23	14.86	605.9	220.8	119.3	315.3

* First crop—soybean.
Second crop—barley.
Third crop—corn.

second soil was an acid silt loam soil from an old abandoned field near South River, New Jersey. This soil is classified as "Elkton silt loam." The Elkton silt loam showed a lime requirement of 3200 pounds by the Veitch method.

The materials[6] (> 200-mesh) were carefully weighed and mixed with the air-

[6] Analyses of materials used: CaO
                                                                              per cent
  Calcium oxide.. 100.00
  Calcium hydrate.. 75.28
  Ground limestone.. 56.52
  Di-calcium silicate... 50.93
  Limosil:
    Total... 40.95
    Free.. 13.05

dried soils before water was added. Sufficient CaO was added in the form of the various materials to meet the lime requirement by the Veitch method.

Applications of calcium oxide equivalent to the free lime in the limosil (as indicated in the analyses) were made in order to ascertain if the value of the limosil was dependent on its content of free lime alone or if the calcium silicate also supplied the base. No additions of fertilizing materials were made to the soils.

TABLE 4

Relative dry weights of buckwheat and soybean plants grown on a Sassafras loam and an Elkton silt loam treated with 5 forms of lime on an equivalent lime (CaO) basis

TREATMENT	EQUIVALENT APPLICATION OF CaO PER ACRE	RELATIVE DRY WEIGHT		AVERAGED RELATIVE DRY WEIGHT, BOTH CROPS	AVERAGED RELATIVE DRY WEIGHT, BOTH CROPS ON BOTH SOILS	AVERAGED RELATIVE DRY WEIGHT, BUCKWHEAT	AVERAGED RELATIVE DRY WEIGHT ,SOYBEANS
		Buckwheat	Soybean				
Sassafras loam							
		(4.49 gm.)	(4.86 gm.)				
No lime............................		100.0	100.0	100.0	100.0	100.0	100.0
3.6117 gm. calcium oxide............	2,000	141.1	190.0	165.5	256.6	352.8	160.5
4.7976 gm. calcium hydrate..........	2,000	188.8	180.2	184.5	260.5	364.9	156.0
6.4302 gm. ground limestone.........	2,000	218.7	160.5	189.6	251.7	344.9	158.5
7.0916 gm. di-calcium silicate........	2,000	212.8	168.6	190.7	303.1	423.4	182.7
8.8197 gm. limosil..................	2,000	200.8	178.4	189.6	289.7	395.8	183.5
*0.4713 gm. calcium oxide...........		90.9	113.0	101.9	160.9	199.5	122.2
Elkton silt loam							
		(1.58 gm.)	(4.39 gm.)				
No lime............................		100.0	100.0	100.0			
5.8000 gm. calcium oxide...........	3,200	564.5	130.9	347.7			
7.7126 gm. calcium hydrate.........	3,200	541.0	131.8	336.4			
10.2726 gm. ground limestone........	3,200	471.0	156.5	313.8			
11.4013 gm. di-calcium silicate.......	3,200	634.0	196.8	415.4			
14.1785 gm. limosil.................	3,200	590.0	188.5	389.7			
*1.8500 gm. calcium oxide...........		308.2	131.3	219.8			

* Equivalent to the free CaO in limosil.

A crop of buckwheat (4 plants per pot) was planted on December 10, 1921, and harvested 16½ weeks later. The buckwheat was followed by soybeans, which were planted on April 7, 1922, and harvested after 12½ weeks. The relative dry weights are given in table 4.

On the Sassafras loam, the ground limestone and di-calcium silicate produced the largest yields of buckwheat; but uniform results were obtained with soybeans. On the Elkton silt loam, the buckwheat grew best in the pots treated

with di-calcium silicate. The soybeans were most favorably effected by di-calcium silicate and limosil. However, considering the averaged results, there is very little difference between the results from the different materials, with the possible exception of di-calcium silicate which produced somewhat larger average yields than the other materials.

A comparison of the yields from the soils treated with limosil, with those obtained from the soils treated with CaO equivalent to the free lime in limosil, shows that the base in combination with the silica is also efficacious in neutralizing the unproductive factors of acid soils.

Series IV

A field experiment for a test of the comparative effects of the various forms of lime used in the controlled experiments described above was arranged and carried out on 12 plots in 1921 and 1922. Each plot was 16 feet by 13 feet 7 inches ($\frac{1}{200}$ acre each) with a path of 2 feet between plots. The experiment was carried out on a low, rather poorly drained portion of a field. The soil was acid to litmus and was overgrown with weeds at the time the experiment was started in May. The soil is usually classified as a Sassafras loam, and is the same as that of the New Jersey plot experiments.

A general fertilizer treatment of acid phosphate at the rate of 300 pounds per acre and muriate of potash at the rate of 50 pounds per acre was made to the plots. Five treatments of different liming materials[7] were made in duplicate on May 9, 1921. These materials were added at the rate of 1000 pounds of CaO per acre. They were thoroughly worked into the soil with a disc harrow. Soybeans were planted on June 27, and harvested on October 4, 1921. Without further treatment to the soil, buckwheat was planted as the 1922 crop. It was planted on May 15 and harvested on July 21. The paths between the plots were cut wider in the harvest of this crop, but due allowance has been made in calculating the results. The application of the various materials used and the green weights (average of 2 plots), together with the calculated yields per acre and the relative yields are given in table 5.

The ground limestone and di-calcium silicate show better results with the soybeans, while the other materials are very like in their effect on the growth of this plant. The most striking result with the buckwheat is the very low relative yield obtained with the limosil. The averaged relative yields of the 2 crops show that ground limestone, calcium hydrate and di-calcium silicate are about equally effective, while limosil and the Medford residue lime are decidedly lower.

[7] Analyses of materials used:

	CaO per cent
Ground limestone	50.00
Calcium hydrate	74.23
Di-calcium silicate	52.20
Limosil	40.95
Medford residue lime	15.92

As a further test of the comparative effects of ground limestone, calcium hydrate and limosil on plant growth, a field experiment was conducted on a Penn loam soil. The field had been under grape culture for several years and was decidedly acid. Plots 18 by 70 feet with 3-feet paths were laid out.

TABLE 5

Yields and relative yields of soybean and buckwheat crops grown on small plots

TREATMENT	1921 CROP SOYBEANS			1922 CROP BUCKWHEAT			AVERAGED RELATIVE YIELD, BOTH CROPS
	Aver-aged yield per plot*	Calcu-lated yield per acre	Rela-tive yield	Aver-aged yield per plot†	Calcu-lated yield per acre	Rela-tive yield	
	pounds	*tons*		*pounds*	*tons*		
No lime..........................	39.75	3.98	100.0	19.00	2.19	100.0	100.0
Calcium carbonate.................	54.88	5.49	138.0	29.13	3.31	153.3	145.7
Calcium hydrate..................	48.38	4.84	121.7	29.75	3.43	156.6	139.2
Di-calcium silicate.................	54.50	5.45	137.1	27.30	3.14	143.7	140.4
Limosil..........................	48.13	4.81	121.1	20.13	2.32	105.9	113.5
Medford residue lime..............	49.33	4.93	124.1	23.63	2.72	124.1	124.3

All lime treatments made at rate of 1000 pounds CaO per acre.

* Average of 2 plots—16 feet by 13 feet 7 inches, or $\frac{1}{200}$ acre each.

† Average of 2 plots—14 feet by 13 feet 7 inches, or $\frac{1}{230.4}$ acre each.

TABLE 6

Relative yields of crops grown on small plots of Penn loam on College Farm

TREATMENT	SOYBEAN*			CORN*			OATS† AND BARLEY	AVER-AGE ALL CROPS
	Beans	Stalks	Aver-age	Grain	Forage	Aver-age		
	(11.81 bushels per A.)	*(1132 pounds per A.)*		*(88.3 bushels per A.)*	*(4542.5 pounds per A.)*		*(2047.1 pounds per A.)*	
No lime.....................	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ground limestone.............	213.9	191.3	202.6	118.6	113.9	116.3	129.5	149.5
Calcium hydrate..............	203.2	166.8	185.0	112.8	88.6	100.7	179.5	155.1
Limosil.....................	188.1	166.8	177.5	131.4	106.3	118.9	153.3	149.9

Applications of liming materials at rate of 2000 pounds CaO per acre.

* Plots 18 feet by 21 feet, or $\frac{1}{115}$ acre each.

† Plots 18 feet by 13 feet, or $\frac{1}{186.1}$ acre each.

Applications of ground limestone, calcium hydrate, and limosil were made at the rate of 2000 pounds of CaO per acre without fertilizer.

These larger plots were divided into smaller areas depending upon the crop planted, permitting 3 crops for each of the several liming materials. One area was seeded to each: oats and barley mixture, soybeans, and corn. The

oats and barley mixture was planted on May 2, and harvested on July 21, 1922. The soybeans and corn were planted May 25 and harvested on October 20, 1922. The beans were thrashed and the weight of the stalks and beans determined separately. The corn was dried and shelled. The relative yields with the calculated yield per acre of the unlimed plots are given in table 6.

The crop increase on the limed soil over that of the untreated is quite marked in every instance, except that of the corn plot treated with calcium hydrate. Taking all the crops into consideration it is interesting to note that the difference in the average relative yields of the 3 crops is easily within the error of this type of experimentation, with no determined advantage of one material over the other. This is in entire accord with the previously described pot experiments.

CONCLUSIONS

The growth of several plants as influenced by equivalent applications of lime in various forms, on several acid soils, has been studied under controlled conditions (pot experiments) and also by means of field experiments. The studies were made with particular reference to calcium silicates as possible carriers of lime. The following are the general conclusions from the studies:

1. As a whole, the artificial calcium silicates were as effective as the common forms of lime in overcoming the unproductive condition of so-called "acid" soils when applied on an equivalent CaO basis.

2. The greatest deviation from the above generalization occurred in the exceptional increase in the growth of barley on soils treated with di-calcium silicate. The greater barley yields obtained with the silicate might possibly be due to the greater absorption of the silicon of the silicate, resulting in a healthier and heavier plant.

3. The percentages of nitrogen in the soybean, barley, and buckwheat plants varied with the soil, the higher percentages having been found under the more unfavorable conditions of the untreated or so-called "acid" soils. The treatments of limestone, calcium hydrate and di-calcium silicate gave crops of closely comparable nitrogen content. The greatly enhanced growth on the limed soils always netted a greater recovery of nitrogen.

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